PB87-140349

Measurement of Hydrolysis Rate Constants for Evaluation of Hazardous Waste Land Disposal Volume 1. Data on 32 Chemicals

(U.S.) Environmental Research Lab., Athens, GA

Prepared for

Technology Applications, Inc., Athens, GA

Dec 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-140349

EPA/600/3-86/043
December 1986

MEASUREMENT OF HYDROLYSIS RATE CONSTANTS FOR EVALUATION OF HAZARDOUS WASTE LAND DISPOSAL
Volume 1. Data on 32 Chemicals

by

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ATHENS, GEORGIA 30613

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/3-86/043	2.	3. RECIPIENT'S ACCESSION NO. PB87 140349/AS
4. TITLE AND SUBTITLE MEASUREMENT OF HYDROLYSIS RATE CONSTANTS FOR EVALUATION OF HAZARDOUS WASTE LAND DISPOSAL, Volume 1: Data on 32 Chemicals		5. REPORT DATE December 1986 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) J.Jackson Ellington, Frank E. Stancil, Jr., and William D. Payne		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, GA 30613 *Technology Applications, Inc., Environmental Research Laboratory, Athens, GA 30613		10. PROGRAM ELEMENT NO. ABWD1A 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Research Laboratory - Athens, GA Office of Research and Development U.S. Environmental Protection Agency Athens, GA 30613		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/01

15. SUPPLEMENTARY NOTES

16. ABSTRACT

To provide input data for a mathematical model to estimate potential groundwater contamination form chemicals in land disposal sites, hydrolysis rate constants were determined for 26 regulated chemicals under carefully controlled conditions. Hydrolysis rates were measured under sterile conditions at precisely controlled temperatures and at three pH levels. Conditions were adjusted to provide sufficiently precise rate constants to meet modeling requirements determined through model sensitivity tests. In addition to close monitoring of temperature and pH, precautions were taken to minimize impact of adventitious processes. Chemical concentrations as a function of incubation time were measured by gas chromatography, liquid chromatography, or ion exchange chromatography. Identities and purities of the chemicals were determined by mass spectrometry supplemented, in some cases, by infrared spectrometry.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT "RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 131
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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FOREWORD

As environmental controls become more expensive and penalties for judgment errors become more severe, environmental management requires more precise assessment tools based on greater knowledge of relevant phenomena. As a part of this Laboratory's research on occurrence, movement, transformation, impact, and control of chemical contaminants, the Measurements Branch determines the occurrence of unsuspected organic pollutants in the aquatic environment and develops and applies techniques to measure physical, chemical, and microbial transformation and equilibrium constants for use in assessment models and for development of property reactivity correlations.

In implementing the land banning provision of the 1984 Hazardous and Solid Waste Amendments to PL 98-616 (RCRA), a mathematical model was developed to estimate potential groundwater contamination from chemicals in land disposal sites. Application of the model requires as input the hydrolysis rate constant(s) for the chemical of concern. This report documents the laboratory measurement of hydrolysis rate constants for 26 compounds regulated under RCRA. Approximately three thousand chemical analyses were required on 29 different organic compounds (including standard reference compounds) to perform the rate constant measurements. Experimental conditions were selected and carefully controlled to provide sufficiently precise rate constants to meet the requirements resulting from model sensitivity tests.

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ABSTRACT

To provide input data for a mathematical model to estimate potential groundwater contamination from chemicals in land disposal sites, hydrolysis rate constants were determined for 26 regulated chemicals under carefully controlled conditions. Hydrolysis rates were measured under sterile conditions at precisely controlled temperatures and at three pH levels (3,7, and 11). Conditions were adjusted to provide sufficiently precise rate constants to meet modeling requirements determined through model sensitivity tests. In addition to close monitoring of temperature and pH, precautions were taken to minimize impact of adventitious processes. Chemical concentrations as a function of incubation time were measured by gas chromatography, liquid chromatography, or ion exchange chromatography. Identities and purities of the chemicals were determined by mass spectrometry supplemented, in some cases, by infrared spectrometry.

Hydrolysis rates for three standard reference compounds (chlorostilbene oxide for acid, 2,4-D methyl ester for base, and benzyl chloride for neutral conditions) were measured repetitively to assess the effect of undetected changes in experimental conditions. Pseudo-first order rate constants determined for benzyl chloride at 28.0°C over 8 months had a coefficient of variation (C.V.) of 9.0%. Values determined at higher temperatures (36.4, 45.0, and 52.9°C) and extrapolated back to 28.0°C had a C.V. of 18.0%. Second-order rate constants for the 2,4-D methyl ester and for 4-chlorostilbene oxide determined under similar conditions (28.0°C, 8 mo.) had C.V.'s of 14.7% and 14.0%, respectively.

Hydrolysis rate constants were determined experimentally for the following 26 compounds: warfarin, aldrin, brucine, dieldrin, disulfoton, endosulfan I, endosulfan II, fluoroacetic acid sodium salt, 2-methyllactonitrile, famphur, acrylamide, acrylonitrile, cis-1,4-dichloro-2-butene, trans-1,4-dichloro-2-butene, 4,4-methylene-bis-(2-chloroaniline), pentachloronitrobenzene, pronamide, reserpine, thiourea, uracil mustard, ethyl carbamate, 2,3-dichloropropanol, 1,3-dichloropropanol, 1,2,3-trichloropropane, 1,2,3-trichlorobenzene, and 1,2,4-trichlorobenzene. Rate data was also reported for: nitrobenzene, mitomycin C, chloromethyl methyl ether, 1,2-dibromo-2-chloropropane, and ethylene dibromide.

All compounds except thiourea were hydrolyzed to some extent under the varying conditions of pH and temperature employed. Hydrolysis rate constants reported at 25°C ranged from approximately 1 hr^{-1} to 1 x 10^{-7} hr^{-1}. Half-lives correspondingly ranged from a few minutes to centuries.

This report covers a period from October 1985 to July 1986, and work was completed as of July 1986.

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ACKNOWLEDGMENTS

This work was conducted at the Athens Environmental Research Laboratory through the combined efforts of EPA, Technology Applications, Inc. (TAI), and University of Georgia (UGA) personnel. The technical assistance of Ms. Cheryl Trusty (UGA) and Miss Sarah Patman (UGA) is gratefully acknowledged. Mr. Alfred Thruston, Dr. John McGuire, and Dr. Timothy Collette generated the chemical spectral data (Appendices A and B) needed to verify identity and estimate purity. The assistance of Mr. Heinz Kollig in literature searches for hydrolysis data and methods of analysis was very nelpful in the initial stages of the project. The assistance of Dr. Lee Wolfe and Mr. Lee Mulkey throughout the project and including review of this report is gratefully acknowledged. Discussions with Mr. William Donaldson were always fruitful and are so acknowledged. Mrs. Elaine McCarity's effort in typing the draft and subsequent revisions was exemplary.

SECTION 1

INTRODUCTION

1.1 Purpose

In implementing the 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act (RCRA), EPA's Office of Solid Waste (OSW) will apply a decision rule based on a mathematical model to chemicals under consideration that considers horizontal underground movement of a chemical based on advection, dispersion, sorption, and chemical hydrolysis. Application of the model requires as input the second-order or first-order hydrolysis rate constants for chemicals containing hydrolyzable functional groups. A total of 362 compounds, divided into three groups, are to be regulated initially. This report provides first- and second-order hydrolysis rate constants for those organic compounds in the first group for which satisfactory values were not developed in an earlier evaluation process and describes the laboratory experiments conducted to measure hydrolysis rate constants (1).

1.2 Background

The Hazardous and Solid Waste Amendments of 1984 to PL 98-616 (RCRA) stipulate that land disposal of "hazardous wastes" is prohibited unless the EPA Administrator determines that prohibition of some wastes is not required to protect human health and the environment because those particular wastes are not likely to reach unacceptable levels in groundwater as a result of land disposal. The amendments define hazardous waste as any of 362 specific compounds (either part of or inclusive of Appendix VIII compounds). In compiling this list, major considerations were toxicity of the material and quantity of waste material generated annually.

To provide a practical tool for determining which listed hazardous materials may be disposed of by land disposal and under what conditions, the use of a relatively simple model was suggested that would estimate potential groundwater contamination for each listed chemical. The model considers horizontal movement based on advection, dispersion, sorption, and transformation. Hydrolysis is the only transformation process specifically considered. Although other transformation processes, such as microbial degradation and chemical reduction, may take place, they are not presently included in the model. The model assumes no unsaturated zone for groundwater and assumes saturated groundwater "zones" ranging from 3 meters to 560 meters in depth. The mean depth of those considered is 78.6 meters. Organic carbon contents used in the model will range from 1% to 0.1%. The point at which the groundwater must meet standards may vary but was orignally set at 150 meters horizontally from the point of introduction.

For each chemical considered, the maximum allowable concentration for the receiving groundwater, 150 meters "downstream," is entered into the model, which assumes environmental characteristics for selected subterranian systems. The concentration of leachate leaving the disposal site is computed for various conditions of rainfall, soil type, pH, etc. A computed leachate concentration that would cause unacceptable groundwater conditions is selected by OSW as the

maximum allowable concentration in leachates. A chemical may be disposed of by land only if treatment brings the leachate concentration down to the level selected that would not cause groundwater to exceed the acceptable concentration. The modeling approach applies to landfills, surface impoundments, waste piles, and land treatment operations. Land treatment operations may be addressed in a different manner to allow for reduction in concentrations resulting from the land treatment process.

It is necessary to acquire octanol/water partition coefficients and hydrolysis rate constants for each of the 362 chemicals except for solvents ("fast track" in the list), which will be treated as non-degrading, non-sorbing constituents and chemicals already banned by the State of California (listed as "California"). These two groups comprise 21 and 44 chemicals, respectively. The remainder of the 362 chemicals were separated into 3 groups by OSW: 81 in the "first third," 121 in the "second third," and 95 in the "third third." Rate constant and partition coefficient data are required for these three groups by 7/86, 5/87, and 4/88, respectively. Partition coefficient data are reported in a companion document and have corresponding delivery dates.

Hydrolysis of the organic compounds on the OSW list of chemicals was addressed by a working group of four experts assembled at the Environmental Research Laboratory, Athens, GA, on April 25 and 26, 1985. The experts were chosen for their extensive theoretical and experimental knowledge and experience in the area of chemical reactivity of organic compounds in water. The work group consisted of Dr. N. Lee Wolfe, U.S. Environmental Protection Agency, Athens, GA; Dr. Robert Taft, University of California, Irvine, CA; Dr. Clifford Bunton, University of California, Santa Barbara, CA; and Dr. William Mabey, Kennedy/Jencks Engineers, San Francisco, CA.

The panel addressed only the organic compounds on the list of 362 chemicals provided by OSW. The inorganics included on the list were not addressed. The inorganics will be examined by another group and reported under a separate task. For the organometallic compounds on the list, the panel did not attempt to estimate data, but did provide experimental rate data where available.

The evaluative procedure the panel followed was to divide the compounds into three categories: those that had no hydrolyzable functional groups, those that would hydrolyze with half-lives greater than a year, and those that would hydrolyze with half-lives of less than a year. Hydrolysis rate data were provided for some of the chemicals on the list. The present report was concerned with developing hydrolysis rate data for the remainder.

Of the 81 compounds in the "first third," 54 are either inorganic, contain no hydrolyzable functional group, contain a hydrolyzable functional group that was judged by experts to be non-labile, or have acceptable literature values for hydrolysis reported by Wolfe (1). The determination of acceptable first- or second-order hydrolysis rate constants for the remaining 27 compounds is described in the text of this report.

Table 1 lists the chemical name and Chemical Abstract Number (CAS) as supplied by OSW in the same order as in the OSW listing. The CAS number was used as the definitive chemical descriptor when there was any ambiguity in relating the name of the chemical to the structure of the compound. The expert panel did not have time to conduct an extensive search of the literature because

TABLE 1. CHEMICALS FROM OSW "FIRST THIRD" LIST

CAS Number	Chemical
81-81-2	Warfarin
309-00-2	Aldrin
357-57-3	Brucine
60-57-1	Dieldrin
298-04-4	Disulfoton
115-29-7	Endosulfan[a]
62-74-8	Fluoroacetic Acid, Sodium Salt
75-86-5	2-Methyllactonitrile
55-63-0	Nitroglycerine
52-85-7	Famphur
79-06-1	Acrylamide
107-13-1	Acrylonitrile
50-07-7	Mitomycin C
107-30-2	Chloromethyl Methyl Ether
106-93-4	Ethylene Dibromide
764-41-0	1,4-Dichloro-2-Butene[b]
101-14-4	4,4-Methylene-bis-(2-Chloroaniline)
82-68-8	Pentachloronitrobenzene
92-12-8	1,2-Dibromo-3-chloropropane
23950-58-5	Pronamide
50-55-5	Reserpine
62-56-6	Thiourea
66-75-1	Uracil Mustard
51-79-6	Ethyl Carbamate
616-23-9	2,3-Dichloro-1-propanol and Dichloropropanols[c] N.O.S.
96-18-4	1,2,3-Trichloropropane
12002-48-1	Trichlorobenzene[d]

a Rate determined for Endosulfan I and Endosulfan II
b Rate determined for cis and trans isomers
c Rate determined for 1,3-Dichloro-2-propanol
d Rate determined for 1,2,3-Trichlorobenzene and 1,2,4-Trichlorobenzene

of the number of compounds and short time period. Before beginning laboratory measurements, we, therefore, conducted a three-pronged search of the literature. The literature was searched for methods of chemical analysis, laboratory generated hydrolysis values, as well as protocols to follow in laboratory generation of hydrolysis data. The literature searches were conducted either manually or electronically through use of DIALOG, a database management system that yields access to over 200 databases. Acceptable hydrolysis data was found for nitroglycerine (2), chloromethyl methyl ether (3), ethylene dibromide (4), 1,2-dibromo-3-chloropropane (5), and mitomycin C (6). Data are summarized in the data sheets (Section 5.3).

Suggested screening protocols and detailed test protocols for hydrolysis of chemicals in water were reported by Mabey et al. (7). Suffet et al. (8) suggested refinements to the above hydrolysis protocols. Neither source documented detailed laboratory methods to apply the suggested protocols; however, the suggested protocols were based on present knowledge of the theory and experimental aspects of hydrolysis and, therefore, provided a good foundation to initiate the laboratory determination of hydrolysis rate constants for the OSW chemicals. The methods used for generation of the reported data evolved after consideration of the two documents and discussions with Dr. Lee Wolfe, Athens ERL.

The concept of standard reference compounds (SRC) evolved from discussions with Dr. Wolfe, Mr. William T. Donaldson, and Mr. Heinz Kollig all of Athens ERL. Standard reference compounds are compounds that are used as quality assurance standards and as references in inter-laboratory generation of hydrolysis data. Repetition of rate constant measurement for these compounds over the course of the reporting period established baseline information for evaluating experimental techniques and for all aspects of quality assurance. Three compounds were selected; one for each process: acid, base, and neutral hydrolysis (Section 3.1). Each standard reference compound is also amenable to analysis by both gas chromatography and liquid chromatography. Reproduction of the hydrolysis constants of the SRCs at the established concentrations, pHs, and temperatures insured that the experimental conditions for each set of compounds were acceptable and the rate constants for the OSW compounds could be determined with required precision and accuracy. Tables 2 through 4 (Section 5.5.2) contain SRC rate constant data generated during laboratory determinations of rate constants of the OSW compounds. A range of pseudo-first-order hydrolysis rates for all SRCs and second-order rate constants for the acidic and basic reference compound were established from these determinations. Hydrolysis data for the second and third set of compounds will be reported in subsequent volumes.

1.3 References for Section 1

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SECTION 2

HYDROLYSIS KINETICS

2.1 Hydrolysis Mechanism

Hydrolysis of organic compounds refers to reaction of the compound with water in which bonds are broken and new bonds with HO- and H- are formed. A common example is the reaction of an alkyl halide with the loss of halide ion (-X):

$$RX + HOH \longrightarrow ROH + HX \text{ (or } H^+, X^-)$$

The rate of the reaction may be promoted by the hydronium ion (H^+, or H_3O^+) or the hydroxyl ion (OH^-). The former is referred to as specific acid catalyis and the latter as specific base catalysis. These two processes together with the neutral water reaction were the only mechanisms considered in this study. This allowed direct measurement of the H_3O^+ or OH^- concentration through accurate determination of solution pH.

Some chemicals show a pH dependent elimination reaction:

$$-\overset{H}{\underset{|}{C}}-\overset{X}{\underset{|}{C}}- \xrightarrow[OH^-]{H^+ \text{ or}} C = C + HX$$

In this study only the disappearance of substrate was monitored with no attempts to identify mechanisms.

2.2 Rate Laws

If all processes referred to in Section 2.1 are included where the rate of hydrolysis is given by the equation,

$$-\frac{d[C]}{dt} = k_h[C] = k_A[H^+][C] + k_B[OH^-][C] + k_N'[H_2O][C] \qquad (2.1)$$

where [C] is the concentration of reactant and k_h is the pseudo-first-order rate constant at a specific pH and temperature, k_A and k_B are second-order rate constants and k_N' the pseudo-first-order rate constant for the acid, base and neutral promoted processes, respectively. The water concentration is essentially not depleted by the reaction and much greater than [C], thus $k_N'[H_2O]$ is a constant (k_N).

Equation 2.1 assumes each individual rate process is first order in substrate, thus k_h can be defined as:

$$k_h = k_A[H^+] + k_B[OH^-] + k_N \qquad (2.2)$$

Using the autoprotolysis equilibrium expression

$$K_W = [H^+][OH^-] \tag{2.3}$$

equation 2.2 may be rewritten as

$$k_h = k_A[H^+] + \frac{k_B K_W}{[H^+]} + k_N \tag{2.4}$$

Equation 2.4 shows the dependence of k_h on $[H^+]$ and on the relative values of k_A, k_B, and k_N.

As a good approximation, the second-order rate constants for acid hydrolysis and for base hydrolysis can be calculated by dividing the pseudo-first order rate constant obtained at the appropriate pH by the hydronium ion or hydroxyl ion concentration, respectively. The half-life of a chemical at a given pH and temperature can be calculated from equation 2.5, where k_h is the observed rate.

$$t_{1/2} = \frac{0.693}{k_h} \tag{2.5}$$

Data evaluation methods and calculations are discussed in more detail in Section 5.1.

Excellent discussions of the hydrolysis rate laws are provided by Mabey and Mill (1,2).

2.3 Contributing Factors to Hydrolysis Rates

2.3.1 Temperature

Water and oil baths that precisely held temperature were used when experimentally determining rates of hydrolysis (Section 4.4). This removed the contribution of temperature as a variable during the actual experiments.

2.3.2 pH, Buffer Catalysis

NBS calibrations standards were used to calibrate the pH meter before measurements. The pH was usually measured at the temperature of analysis. In regions where only k_A contributes to hydrolysis, K_h will decrease by a factor of 10 for each unit increase in pH. Similarly where only k_B contributes to hydrolysis, K_h will increase by a factor of 10 for each unit increase in pH. k_N is for the pH-independent hydrolysis rate measurement. Buffers (0.005 M) were used to control pH and avoid buffer catalysis (3).

2.3.3 Ionic Strength

Ionic strength, depending on the chemical, can lead either to acceleration or retardation. For this reason concentrations of buffer solutions

were set as low as possible yet high enough to maintain constant pH over the course of the hydrolysis determination. The compound concentration was correspondingly set low, usually 10^{-4} M or less.

2.3.4 Sterility

Sterile conditions was maintained for all studies to prevent microbial degradation of the chemical (Section 4.5).

2.3.5 Sorption

Chemicals analyzed by gas chromatography were extracted from the aqueous layer and glass surfaces with iso-octane. Samples analyzed by liquid chromatography were checked for sorption by emptying the sample container, rinsing the container with acetonitrile, and analyzing the acetonitrile in the same manner as the sample.

2.4 References for Section 2

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SECTION 3

LABORATORY DETERMINATIONS

3.1 Standard Reference Compounds

Three compounds were chosen as candidate standard reference compounds, one each for acid, base, and neutral hydrolysis. The SRC hydrolysis rate constants were determined before analysis of samples and interspersed with laboratory determination of hydrolysis rates of the compounds in Table 1. Because values and experimental conditions for SRC's were being developed concurrently with measurement of the regulated compounds, the interspersion of SRC's was not as uniform as will be the case in future use of SRC's. Pertinent information as to concentration, pH, temperature, and instrument for analysis is tabulated in Tables 2 through 4. The rate values for all three SRCs are in good agreement with literature or calculated values.

3.1.1 Acid SRC

DL-trans-4-Chlorostilbene oxide was selected as a SRC for acid hydrolysis studies. Operating conditions and calculated rates are in Table 2. The chlorine was essential for analysis by the electron capture detector.

3.1.2 Neutral SRC

Benzyl chloride was selected as a SRC for neutral hydrolysis conditions, since the rate is known to be independent of pH below 13. Also, the degradation rate at room temperature is fast enough to allow easy sampling. Table 3 tabulates analytical parameters. Of particular interest is the last column of K_1 values extrapolated from three elevated temperatures.

3.1.3 Base SRC

Methyl-2,4-dichlorophenoxy acetate (2,4-D methyl ester) served as the base SRC candidate. Table 4 contains rate values and corresponding analytical parameters. Data are reported as calculated from analytical runs.

3.2 Rate Studies-OSW Chemicals

Literature values were found for five of the chemicals in Table 1, reducing the number requiring measurement to 22. The CAS No. for four of these compounds, however, was either for a mixture of isomers or nonspecific isomers. Therefore, Endosulfan I and II: cis- and trans-1,4-dichloro-2-butene; 1,3-dichloro-2-propanol; 2,3-dichloro-1-propanol; 1,2,3-trichlorobenzene; and 1,2,4-trichlorobenzene were merged into the list to yield the final 31 chemicals reported on in the data sheets (includes five from literature).

A general description of laboratory operations will be given in the remainder of this section. A typical hydrolysis experiment consisted of preparing a spiking solution of the compound of interest, preparing buffer solutions, transferring spiked buffer to individual "rate point tubes" (15-ml Teflon lined, screw cap, or sealed ampules), then monitoring degradation by sacrificing individual tubes and determining percentage of the substrate remaining.

TABLE 2. HYDROLYSIS DATA FOR DL-TRANS-4-CHLOROSTILBENE OXIDE

Date	Initial Conc. (ppm)	pH	Temp., °C	Method of Analysis	10^{3a} K1[b] (min^{-1})	K2[c] (M^{-1} min^{-1})	K2 Extrapolated[d]
11/1/85	2.3	3.13	28	LC	17.4 ± 0.3[e]	23.5	
11/6/85	2.3	3.10	28	LC	14.4 ± 0.2	18.2	
11/6/85	2.3	3.10	28	LC	14.9 ± 0.6	18.8	
11/6/85	2.3	3.07	28	LC	14.3 ± 0.8	16.7	
11/6/85	2.3	3.07	28	GC	14.6 ± 1.1	17.1	
11/6/85	2.3	3.63	38	GC	16.9 ± 0.6	72.3	22
11/15/85	2.3	3.01	28	LC	20.8 ± 1.7	21.3	
11/15/85	2.3	3.01	28	LC	23.7 ± 2.2	24.2	
11/15/85	2.3	3.59	38	LC	23.5 ± 1.0	91.4	28
11/15/85	2.3	3.59	38	LC	24.5 ± 1.9	95.3	29
11/15/85	2.3	3.01	28	GC	21.1 ± 0.9	21.6	
3/11/86	2	3.06	28	LC	16.9 ± 1.0	19.4	
3/11/86	2	3.06	28	GC	14.3 ± 0.6	16.4	
3/11/86	2	3.06	28	LC	16.9 ± 1.3	19.4	
3/11/86	2	3.06	28	GC	14.3 ± 1.0	16.5	
5/14/86	2	2.99	23	LC	13.8 ± 1.5	12.5	22

a Every listing in column must be multiplied by 10^{-3} to retrieve K
b Pseudo-first-order rate constant from the slope of the line ln % Remaining vs. Time
c Second order constant calculated from pseudo-first-order rate constant
d Extrapolation to 28°C, based on a 10-fold change in rate for 20°C change in temperature
e Standard deviation of the slope

TABLE 3. HYDROLYSIS DATA FOR BENZYL CHLORIDE

Date	Initial Conc. (ppm)	pH	Temp., °C	Method of Analysis	10^{3a} K1[b] (min^{-1})	10^{3a} K1 (min^{-1}) Extrapolated[c]
11/26/85	1.31	7	53	LC	20.3 ± 0.9[d]	1.15
11/26/85	1.31	7	53	LC	19.1 ± 1.8	1.08
11/26/85	1.31	7	53	LC	21.1 ± 0.9	1.20
11/26/85	1.31	7	53	LC	21.6 ± 0.7	1.22
11/27/85	1.31	7	28	LC	1.0 ± 0.0	
11/27/85	1.31	7	28	LC	1.2 ± 0.0	
11/27/85	1.31	7	28	LC	1.1 ± 0.0	
11/27/85	1.31	7	28	LC	1.0 ± 0.0	
11/29/85	1.31	7	45	GC	7.2 ± 0.2	1.03
11/29/85	1.31	7	45	LC	7.2 ± 0.0	1.02
12/2/85	1.31	7	36	GC	3.1 ± 0.2	1.21
12/2/85	1.31	7	36	LC	3.4 ± 0.1	1.28
5/21/86	1.0	7	53	GC	14.0 ± 0.1	.75
5/21/86	1.0	7	53	GC	13.6 ± 0.3	.73
7/2/86	1.0	7	54	GC	15.4 ± 0.1	.82
7/3/86	1.3	7	54	GC	16.0 ± 0.1	.85

a Every listing in column must be multiplied by 10^{-3} to retrieve K
b Pseudo-first-order rate constants from the slope of the line Ln % Remaining vs. Time
c Extrapolation to 28°C based on a 10-fold change in rate for each 20°C change in temperature
d Standard deviation of the slope

TABLE 4. HYDROLYSIS DATA FOR METHYL-2,4-DICHLOROPHENOXY ACETATE

Date	Initial Conc. (ppm)	pH	Temp., °C	Method of Analysis	10^{3}[a] K1[b] (min^{-1})	K2[c] (M^{-1}, min^{-1})	K2 (M^{-1}, min^{-1}) (Extrapolated[d])
10/7/85	5	9.06	28	LC	8.1 ± 0.3[e]	703	
10/7/85	5	9.06	28	GC	7.0 ± 0.4	613	
10/8/85	5	9.65	28	LC	26.2 ± 0.6	586	
10/8/85	5	9.65	28	GC	27.7 ± 1.2	621	
10/9/85	5	7.11	70	LC	11.4 ± 0.5	88300	678
10/9/85	5	7.11	70	GC	10.0 ± 0.3	77400	594
10/11/85	5	9.14	28	LC	12.0 ± 0.5	855	
10/11/85	5	9.14	28	GC	10.3 ± 0.1	744	
10/11/85	5	8.00	48	LC	10.3 ± 0.4	10300	974
10/11/85	5	8.00	48	GC	8.4 ± 0.2	8600	811
3/6/86	5	8.87	25	LC	5.7 ± 0.2	770	1100
3/6/86	5	8.87	25	GC	4.9 ± 0.2	564	796
3/6/86	5	9.10	25	LC	9.0 ± 0.2	755	1100
3/6/86	5	9.10	25	GC	8.0 ± 0.4	627	886
5/12/86	5	9.38	25	LC	23.0 ± 1.0	959	1400
5/13/86	5	9.38	25	GC	22.4 ± 0.9	934	1300
5/12/86	5	9.45	25	LC	24.9 ± 1.4	883	1200
5/13/86	5	9.45	25	GC	22.4 ± 0.8	794	1100
7/2/86	5.4	8.75	31	LC	9.1 ± 0.4	1600	1100
7/3/86	5.4	8.72	31	LC	7.9 ± 0.2	1500	1000

a Every listing in column must be multipled by 10^{-3} to retrieve K
b Pseudo-first-order rate constants from the slope of the line ln % Remaining vs. Time
c Second order constant calculated from pseudo-first-order constant
d Extrapolation to 28°C based on 10-fold change in rate for each 20°C change in temperature
e Standard deviation of the slope

Spiking solutions were prepared by dissolving the substrate in acetonitrile, methanol, or water. The concentration was such that 0.1 ml diluted to 100 ml with buffer gave a substrate concentration that was 1×10^{-5} M or was 50% of the water solubility or less.

Initial hydrolysis runs were performed at pH 3, 7, and 11. Buffers were prepared at these pHs then measured at the temperature of the hydrolysis run. Each run consisted of five or six tubes. Immediate analysis of one tube established the 100% response peak (T_0). Analysis of a second tube within 3 to 6 hours gave a good estimate of sampling frequency for the remaining tubes.

The initial hydrolysis runs were used to set pH and temperature conditions for subsequent rate determinations. The rate determinations were normally performed in triplicate; however, some compounds required more replicates (aldrin, dieldrin) and some less (2-methyllactonitrile).

SECTION 4

EXPERIMENTAL

4.1 Chemicals and Solvents

4.1.1 Source

The EPA repositories at Research Triangle Park, NC, and Las Vegas, NV, were the first choice for chemicals on which hydrolysis rates were measured. Commercial chemical companies were the second sources. The supplier of each chemical is listed on the data sheets in the Section 5.3.

4.1.2 Identity and Purity

Stated purities are listed on the data sheets. The chemicals were analyzed by mass spectrometry for confirmation of the stated identity. The generated mass spectral data are in Appendix A. GC/FTIR was used to characterize the 1,2,3- and 1,2,4-isomers of trichlorobenzene.

4.1.3 Solvents

Solvents were "distilled in glass," Burdick and Jackson solvents either gas chromatograph or HPLC grade, as required by the method of analysis.

4.2 pH Measurement

An Orion Research EA920 pH meter equipped with an Orion Research Δ810300 Ross combination electrode was used for all pH measurements. National Bureau of Standards (NBS) reference standards were used to calibrate and check the pH meter. The pH meter had a stated accuracy of ±0.02 units. The temperature compensation prode was used for all measurements. The pH was measured at the temperature of the hydrolysis rate measurement and adjusted with base or acid to obtain the desired pH.

4.3 Buffers

Buffer stock solutions were prepared at 0.1 M using sterile water as described above. To prepare pH 3 buffer, 0.1 M potassium hydrogen phthalate was diluted to 0.005 M and final pH adjustment made with 0.1 M HCl. The pH 7 buffer was prepared from 0.1 M potassium dihydrogen phosphate diluted to 0.005 M with final pH adjustment using 0.1 N NaOH. Buffers for pHs 9 and 11 were made by diluting 0.1 M sodium phosphate heptahydrate to 0.005 M with final pH adjustment using 0.1 M NaOH.

Buffer stability was tested initially at 0.001 M. Thus, pH 5 and pH 7 buffers held their respective pH's for the test period. The pH 9 buffer (0.001 M) decreased to pH 8.07 after 24 hours and to pH 7.50 after 96 hours. Buffer at a concentration of 0.005 M remained constant at 9.10 ± 0.03 pH units for 25 days. Containers for the experiment were screw cap test tubes using autoclaved (CO_2 free) water was used.

4.4 Temperature Control

Forma Scientific refrigerated and heated baths (Model 2095) were used for temperatures in the range of 2 to 70°C (±0.02°C). A Lauda C-20 oil bath with a stated control accuracy of ±0.01°C and a fine control range of ±0.2°C was used for temperatures above 68°C. Temperatures were measured with American Society for Testing and Materials (ASTM) thermometers, are calibrated by NBS procedures and NBS certified masters. The thermometers were calibrated in 0.1°C increments.

4.5 Sterile Water

Water used in the experiments was unchlorinated ground water that was first processed through a high capacity reverse osmosis unit and a deionizer unit. This "house" deionized water was further purified by passage through a Barnstead Nanopure II deionizer, 4-Module unit with Pretreatment, High Capacity, and Z-Ultrapure cartridges. Water obtained from this unit had a resistance of greater than 16 meg ohms. This double deionized water was autoclaved for 30 min/liter and allowed to cool before use. The sterile water was stored in a sterile-cotton-plugged container until used. All hydrolysis runs were conducted in screw cap tubes. Data from smear plate counts on agar indicated growth as being less than 1 colony per milliliter through 9 days at 25°C and pH of 5, 7, and 9. Sterility checks on the water were performed intermittently.

Buffer solutions were checked for bacterial growth. Buffer solutions, prepared as described above, were transferred at room temperature to screw cap test tubes. One-half were flame transferred, the other half without flaming. A sample (1 ml) from each tube was plated daily, for nine concurrent days on TGE agar. After a 48-hour incubation, no growth was found. This confirmed sterility. Control checks during hydrolysis runs showed no growth.

4.6 Methods of Analysis

Details of the methods of chemical analysis are listed on the data sheet for each compound. Generally gas chromatography was the first method of choice for four reasons:

1) sensitivity and specificity of detectors

2) solvent extraction stopped hydrolysis and allowed multiple injections over extended periods of time

3) solvent extraction also lessened problems caused by compound sorption to glass

4) direct aqueous injection of water soluble compounds that were not amenable to other methods of analysis

High performance liquid chromatography (HPLC) was used extensively; ion chromatography and the diode array UV-detector were used in the analysis of sodium fluoroacetate and thiourea, respectively. Hydrogen cyanide released by the decomposition of 2-methyllactonitrile was monitored by EPA Method 335.

Linearity of detector response in the concentration range of analysis for each chemical was established to ensure reliable concentration versus time plots.

SECTION 5

DATA ANALYSIS AND PRESENTATION

5.1 Data Compilation Methods

Raw data consisted of time of sampling and percentage substrate remaining. The measured concentration at time zero was considered 100% and was the reference point for the remaining points. The data were processed on a Lotus 1-2-3/IBM PC-XT using a data entry/linear regression program. The raw and calculated data were entered in a notebook. Graphs were made by using personal computers to plot ln (% remaining) vs. time and to calculate statistical values.

Values obtained from the linear regression program include the slope (pseudo-first-order rate constant), Y-intercept, variance, SD of Y-intercept, SD of slope, and the correlation coefficient (r^2).

5.2 Standard Reference Compound Data

All the laboratory data on the SRCs are summarized in Tables 2, 3, and 4. Figures 1, 2, and 3 are representative graphical presentations of hydrolysis data for each compound. Figure 4 is an Arrhenius plot for hydrolysis of benzyl chloride at four temperatures. An energy of activation of 22.4 ± 2.3 Kcal/mole for benzyl chloride was calculated from the data associated with Figure 4. An error of 10% in the slope was assumed. The change in the hydrolysis rate constants for benzyl chloride and the methyl ester of 2,4-D after March 1986 illustrates how susceptible rate determinations are to slight changes in the controlled parameters. No plausible explanation has been found for either the increased 2,4-D rate or the decreased benzyl chloride rate.

5.3 Summary Sheets for OSW Chemicals

A summary sheet was prepared for each chemical. The summary sheet contains information pertinent to the analysis of each chemical, and includes source, purity, and analytical method. Also included on the sheet is information on pH, temperature, pseudo-first-order and second-order rate constants, half-lives, and correlation coefficients (r^2). Sample identity was confirmed by mass spectrometry and infrared spectrometry as reported in the Appendices. Where a literature reference for the hydrolysis of a compound was obtained, the summary sheet contains the second-order rate constant if applicable and first-order rate constants at 25°C. For several of the compounds, lab data were generated in this study to fill in gaps in the literature.

Data from all the summary sheets were used to derive the values in Table 5. These values are the calculated rate constants at 25°C. The rate constants were assumed to vary a factor of 10 for each 20°C change in temperature (Ref. 1, Section 1). This corresponds to an activation energy of about 20 kcal/mole. When applicable extrapolated values (25°C) were obtained using activation parameters. A temperature correction was applied to all calculations involving K_w or $[OH^-]$. When statistical tests of the data indicated the hydrolysis was independent of pH, hydrolysis values from the extremes of pH (acid and/or base) were included when calculating the neutral hydrolysis rates reported in Table 5. Confidence limits were calculated from the mean and standard deviation values and are the values reported in Table 5.

TABLE 5. HYDROLYSIS RATE CONSTANTS AND HALF-LIVES AT 25°C

	Rate Constants			Calculated $t_{1/2}$
	Acid $M^{-1}hr^{-1}$	Neutral hr^{-1}	Base $M^{-1}hr^{-1}$	at pH 7
Warfarin	1.4×10^{-4}	4.9×10^{-6}	0.026	16yr
Aldrin		$(3.8\pm2.3)\times10^{-5}$		760d
Brucine	5.9×10^{-3}		0.21	36,000yr
Dieldrin		$(7.5\pm3.3)\times10^{-6}$		10.5yr
Disulfoton		$(2.8\pm0.4)\times10^{-4}$	5.99	103d
Endosulfan I	$(8.1\pm2.7)\times10^{-3}$	$(3.2\pm2.0)\times10^{-3}$	$(1.0\pm0.7)\times10^{4}$	218hr
Endosulfan II	$(7.4\pm3.9)\times10^{-3}$	$(3.7\pm2.0)\times10^{-3}$	$(1.5\pm0.9)\times10^{4}$	187hr
Fluoroacetic Acid Sodium Salt		$<1.7\times10^{-6}$		>47yr
2-Methyllactonitrile		4.47		0.15hr
Nitroglycerine[a]			77±11	10yr
Famphur		$(2.5\pm.9)\times10^{-4}$	5.0	115d
Acrylamide	$<3.6\times10^{-2}$	$<(2.1\pm2.1)\times10^{-6}$		38yr
Acrylonitrile	$(4.2\pm0.3)\times10^{-2}$		$(6.1\pm6.5)\times10^{-1}$	122yr[b]
Mitomycin C[a]		3.7×10^{-4}	3.0±1.7	78hr
Chloromethyl methyl ether[a]		21		2 min
1,2-Dibromo-3-chloropropane[a]			20.6	38±4yr
Ethylene Dibromide[a]		9.9×10^{-6}		8yr
cis-1,4-Dichloro-2-butene		$(9.1\pm1.1)\times10^{-3}$		3.2d
trans-1,4-Dichloro-2-butene		$(9.0\pm0.5)\times10^{-3}$		3.2d
4,4-Methylene-bis-(2-chloroaniline)	$(2.9\pm3)\times10^{-4}$	$<9\times10^{-8}$		>800yr
Pentachloronitrobenzene		$(2.8\pm0.7)\times10^{-5}$		2.8yr
Pronamide	4.3×10^{-3}	$<1.5\times10^{-5}$	7.4×10^{-2}	>700yr
Reserpine	0.82	$(4.5\pm1.8)\times10^{-5}$	9.8±10.9	1.7yr
Thiourea		$<5.3\times10^{-7}$		>150yr
Uracil Mustard		0.57±0.08	$(2.05\pm0.2)\times10^{5}$	1.2hr
Ethyl Carbamate		$<2.6\times10^{-7}$	1.1×10^{-1}	>300yr
2,3-Dichloro-1-propanol		$(5.3\pm0.8)\times10^{-5}$	20.6±2.2	1.4yr
1,3-Dichloro-2-propanol		$(3.1\pm0.2)\times10^{-3}$	854±87	9.3d
1,2,3-Trichloropropane		$(1.8\pm0.6)\times10^{-6}$	9.9×10^{-4}	44yr
1,2,3-Trichlorobenzene		$(1.6\pm1.3)\times10^{-5}$		4.9yr
1,2,4-Trichlorobenzene		$(2.3\pm.9)\times10^{-5}$		3.4yr

[a] Values were extracted from the references in Section 1, the second-order alkaline hyrolysis rate constant for Mitomycin C was determined at Athens ERL.

[b] Calculated from alkaline second-order rate constant assuming zerio neutral contribution.

Constraints of time, personnel, bath space, and availability of instruments of analysis dictated that rate determinations be confined to shorter periods of time (note the half-lives and temperatures in summary sheets). Ideally, decrease in compound concentration was monitored through three half-lives (<12% remaining); as seen in the summary sheets, some compounds decreased <10% during the period of analysis while others decreased to zero concentration.

An illustrative plot on semi-log paper of % Remaining vs. Time is included with applicable data sheets. Included on the sheet are the pseudo-first-order rate constants, half-life, and r^2.

$K_1 = 1.74 \times 10^{-2}\ min^{-1}$

$T_{1/2} = 39.8$ min.

$R^2 = 0.999$

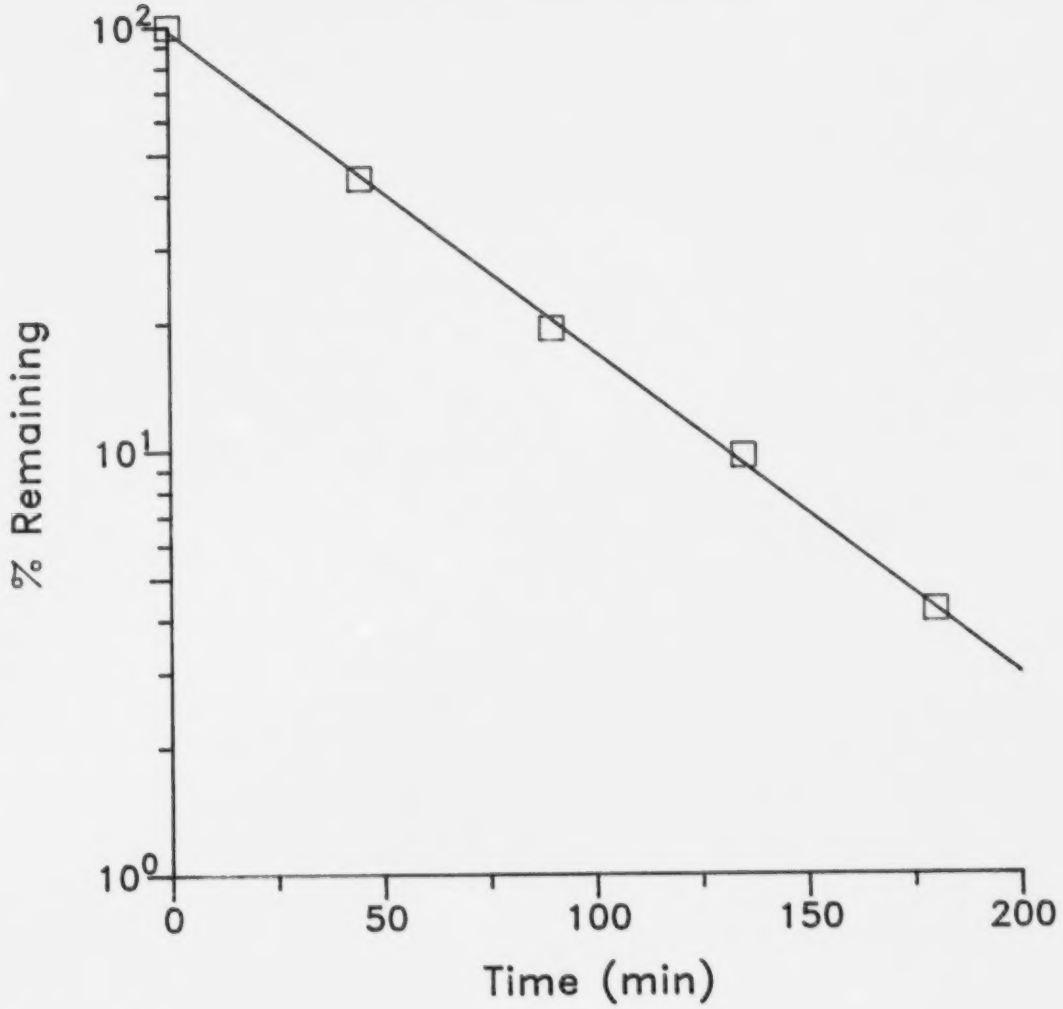


Figure 1. Hydrolysis of DL–<u>trans</u>–4–Chlorostilbene Oxide at 28°C, pH 3.13

$K_1 = 2.04 \times 10^{-2}\ min^{-1}$

$T_{1/2} = 34$ min.

$R^2 = 0.994$

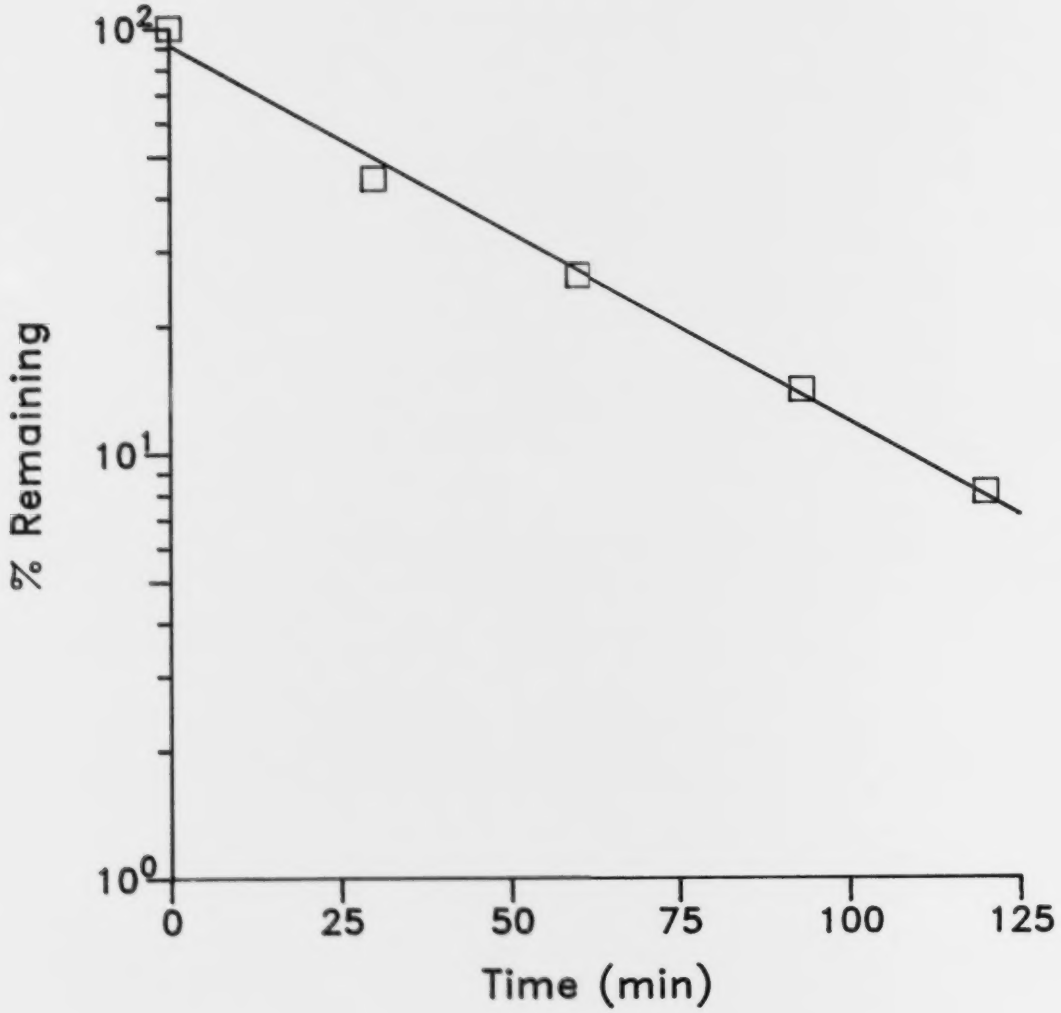


Figure 2. Hydrolysis of Benzyl Chloride at 59.2°C, pH 7.0

$K_1 = 8.07 \times 10^{-3}\ min^{-1}$

$T_{1/2} = 85$ min.

$R^2 = 0.994$

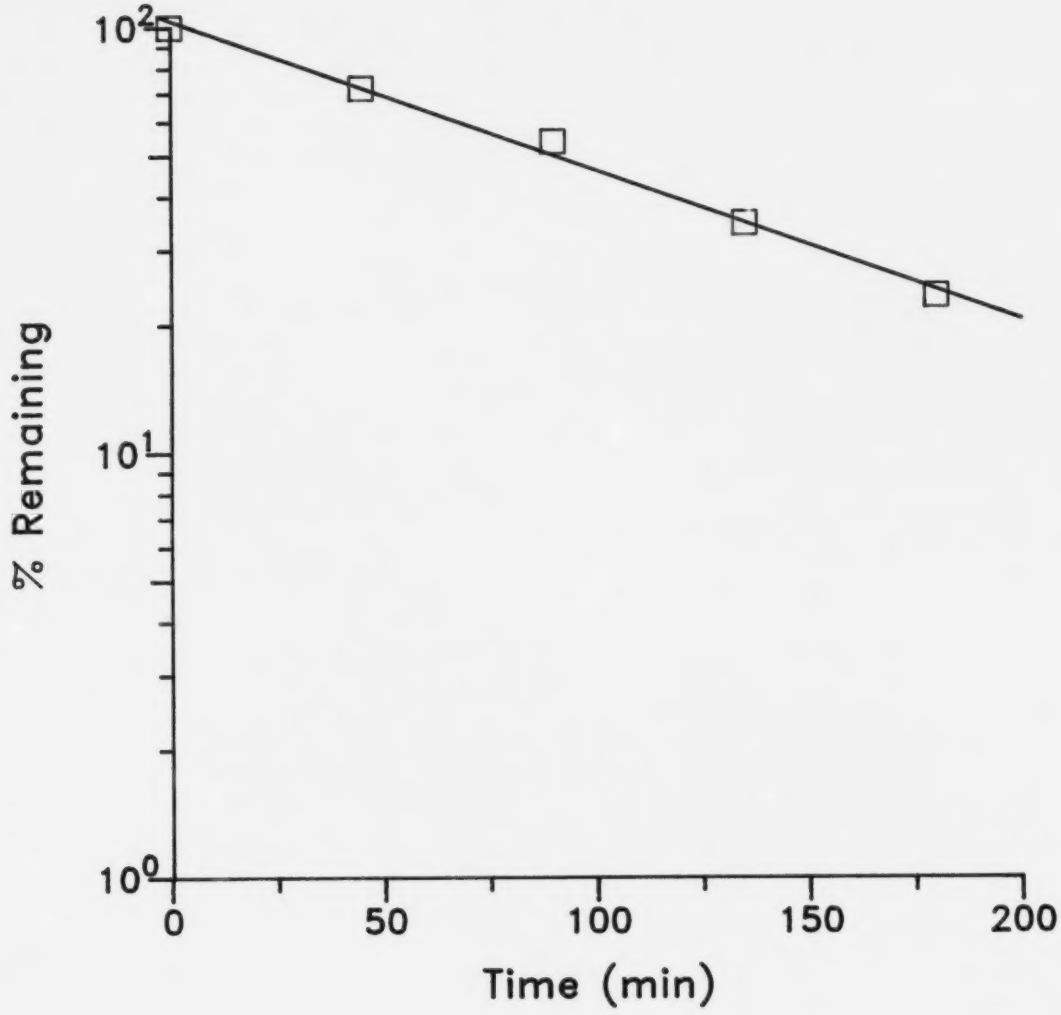


Figure 3. Hydrolysis of Methyl–2,4–Dichlorophenoxy Acetate at 28°C, pH 9.0

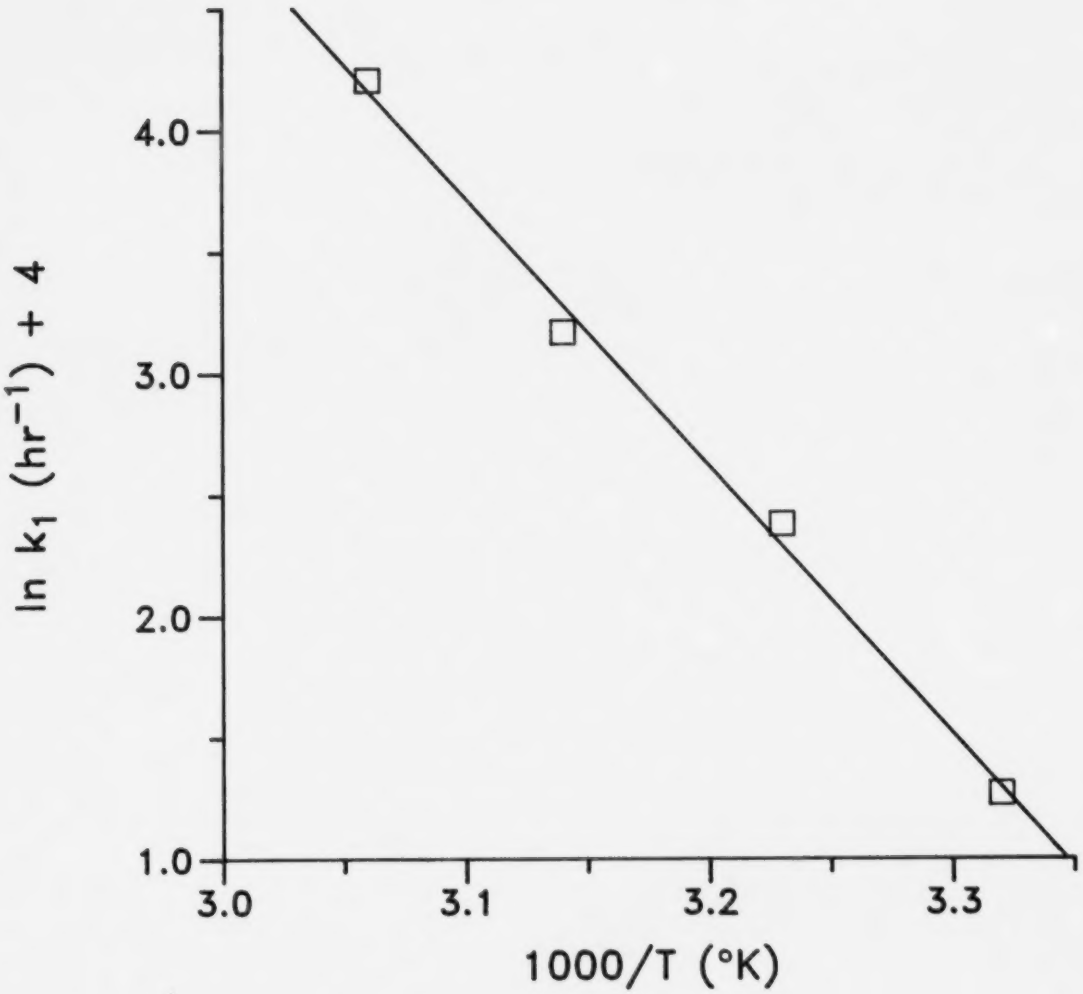


Figure 4. Dependence of Benzyl Chloride Hydrolysis on Temperature

5.3.1 Warfarin
CAS No. 81-81-2

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^3K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.17	87.0	6.0		4.8	0.999
3.09	68.0	2.2		12.9	0.961
7.17	87.0	3.2		9.1	0.997
7.11	68.0	0.5		57.4	0.931
10.18	68.0	1.2		23.9	0.889
9.69	87.0	3.1		9.2	0.998

Comment: Warfarin has an ionizable functional group that may affect the neutral hydrolysis rate constant. The data indicate, however, this effect is quite small over the pH range studied. Activation energies calculated at the three pH's and assuming an error of 10% were 12.9 ± 2.5 Kcal/mole for the acid, 22.2 ± 1.2 Kcal/mole for the neutral, and 26.7 ± 2.5 Kcal/mole for the base hydrolyses, respectively.

Water Solubility: 170 mg/L

Source: RTP Repository

Listed Purity: 95%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 3 ppm

Analytical Procedure: Warfarin was analyzed by direct injection of 20 microliters of neutralized buffer solution onto a Resolvex C-18 column

Extraction Solvent: NA

Instrumentation: GC ___ HPLC X IC ___ Diode Array UV ___

Detector: UV at 282 nm

Column: Resolvex C18, 10 micron, 25 cm x 4.6 mm

Temperature Program: NA

Mobile Phase: 58% 0.005M Tetrabutyl ammonium phosphate (Pic-A), 42% acetonitrile

Internal Standard: NA

Linear Range of Analysis: 0.32 - 3.2 ppm

5.3.1 Warfarin

$K_1 = 6.0 \times 10^{-3}\ hr^{-1}$
$T_{1/2} = 4.8$ days
$R^2 = 0.999$

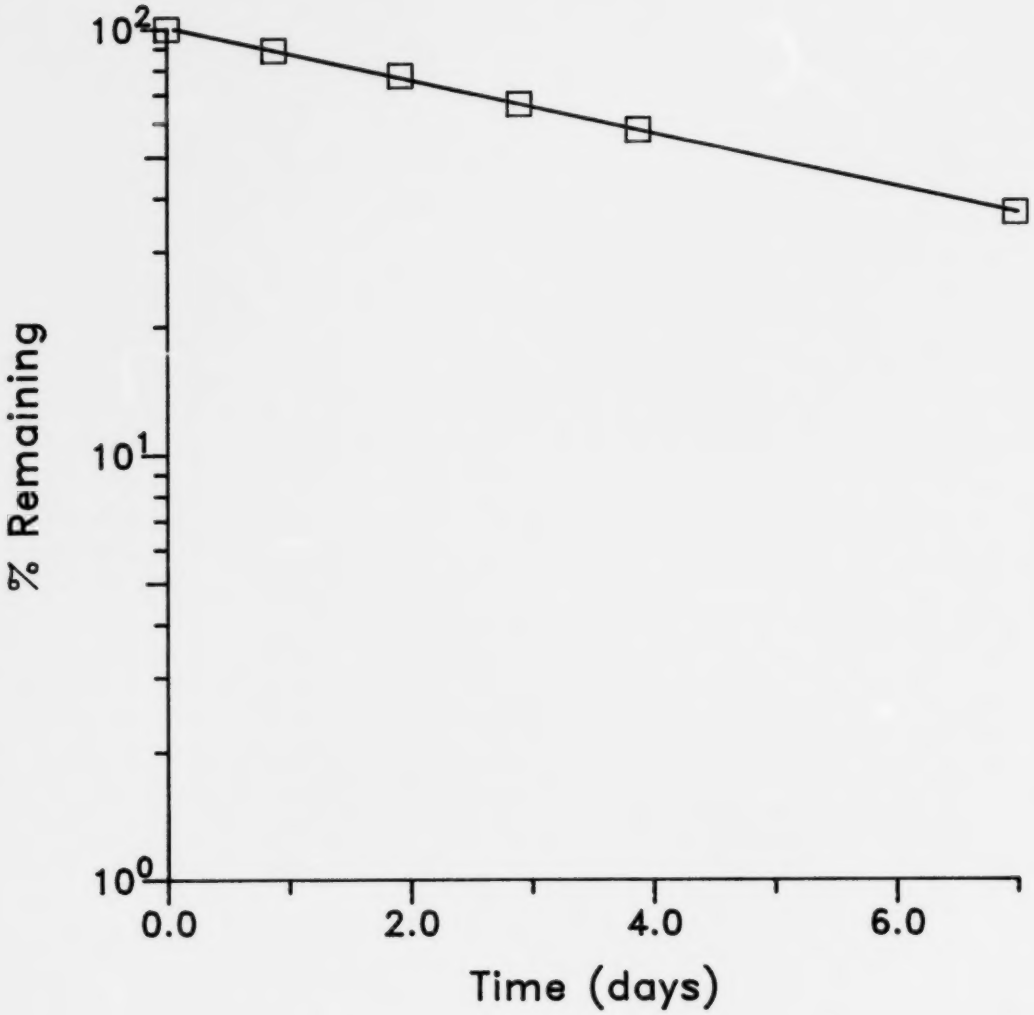


Figure 5.3.1 Hydrolysis of Warfarin at 87°C, pH 3.17

5.3.2 Aldrin
CAS No. 309-00-2

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^2K_1(d^{-1})$	$K_2(M^{-1}d^{-1})$	$t_{1/2}(d)$	r^2
3.03	68.0	36.0[a]		1.9	0.960
3.20	69.0	2.7		25.9	0.995
2.83	72.5	20.0		3.5	0.991
6.99	68.0	24.0		2.9	0.825
7.19	72.5	15.0		4.6	0.632
10.70	68.0	26.4		2.5	0.991
10.19	69.0	4.1		16.8	0.651
10.26	69.0	7.3		9.5	0.973
10.49	69.0	8.4		8.2	0.953
10.64	72.5	10.0		7.0	0.702

[a] Note units of K_1 are d^{-1}

Water Solubility: 0.01 mg/l

Source: EPA

Listed Purity: 99%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 3 ppb

Analytical Procedure: The hydrolysis sample (10 ml) is extracted with 2 ml of a 31 ppb solution of dieldrin in iso-octane. The extract is injected without dilution.

Extraction Solvent: Dieldrin 31 ppb in iso-octane

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: ECD

Column: 30 M DB-5, 1 micron film, 0.32 mm ID

Temperature Program: 200°C Isothermal

Mobile Phase: NA

Internal Standard: Dieldrin 31 ppb

Linear Range of Analysis: 0.1 - 10 ppb

5.3.2 Aldrin

$K_1 = 8.3 \times 10^{-3}\ hr^{-1}$
$T_{1/2} = 3.5$ days
$R^2 = 0.991$

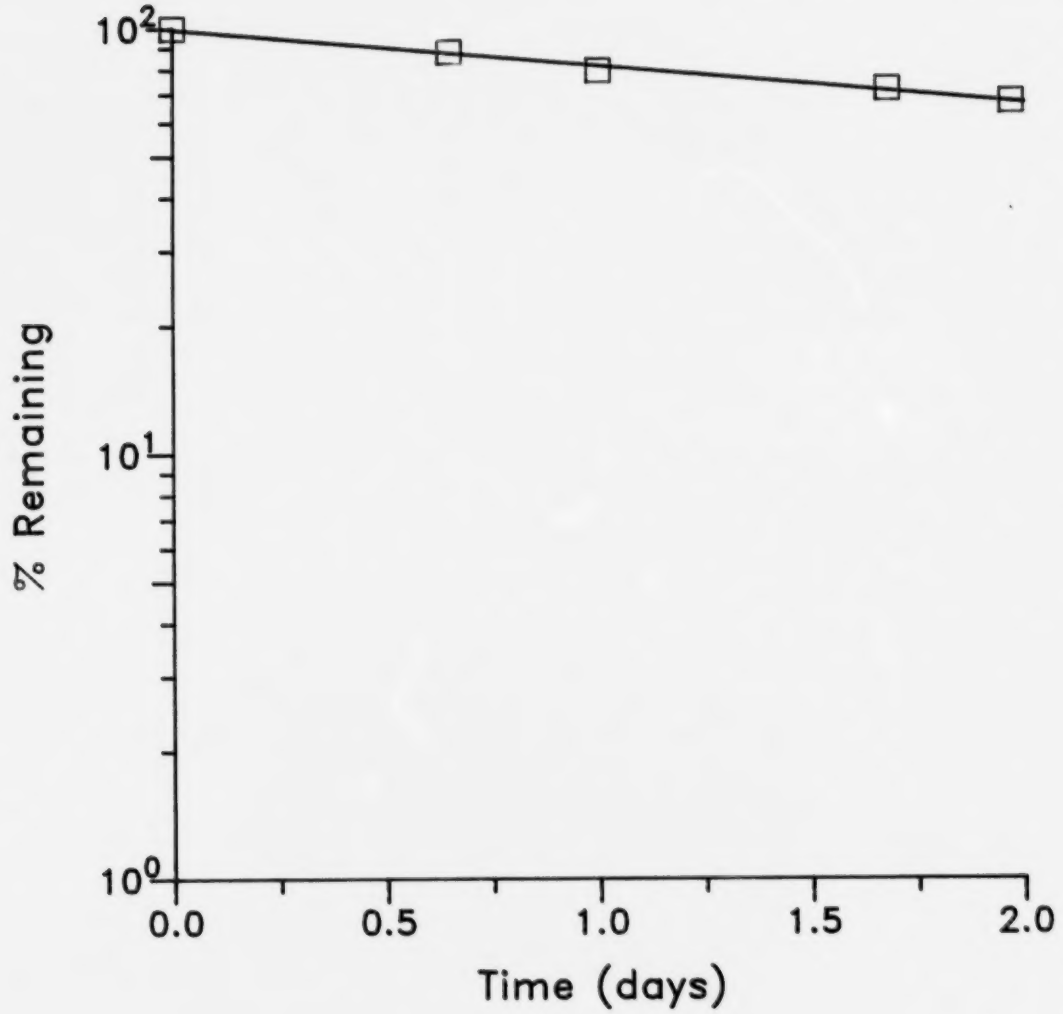


Figure 5.3.2 Hydrolysis of Aldrin at 72.5°C, pH 2.83

5.3.3 Brucine
CAS No. 357-57-3

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^4 K_1 (hr^{-1})$	$K_2 (M^{-1} hr^{-1})$	$t_{1/2}$(d)	r^2
3.10	68.0	6.6	0.8	43.7	.999
10.20	68.0	4.9	0.21	59.5	.925
10.20	68.0	4.8	0.21	59.5	.977
7.08	68.0	<0.5		>570	--
7.16	87.0	6.0		46.0	.959

Comment: The extrapolated half-life is calculated based on the acid and alkaline contribution. The values at pH 7 and elevated temperatures appear too high for amide hydrolysis and were not used in the calculations.

Water Solubility: 758 mg/L

Source: Aldrich

Listed Purity: 98%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 8.7 ppm

Analytical Procedure: Aliquots (20 microliters) were injected onto the HPLC and eluting peaks passed through a UV detector. Quantitation was by peak height.

Extraction Solvent: NA

Instrumentation: GC ___ HPLC X IC ___ Diode Array UV ___

Detector: UV at 263 nm

Column: Resolvex CN or Ultrasphere ODS

Temperature Program:

Mobile Phase: 50/50 methanol/0.005M 1 octanesulfonic acid, pH 3

Internal Standard:

Linear Range of Analysis: 1-10 ppm

5.3.3 Brucine

$K_1 = 6.2 \times 10^{-4}\ hr^{-1}$

$T_{1/2} = 46.6$ days

$R^2 = 0.959$

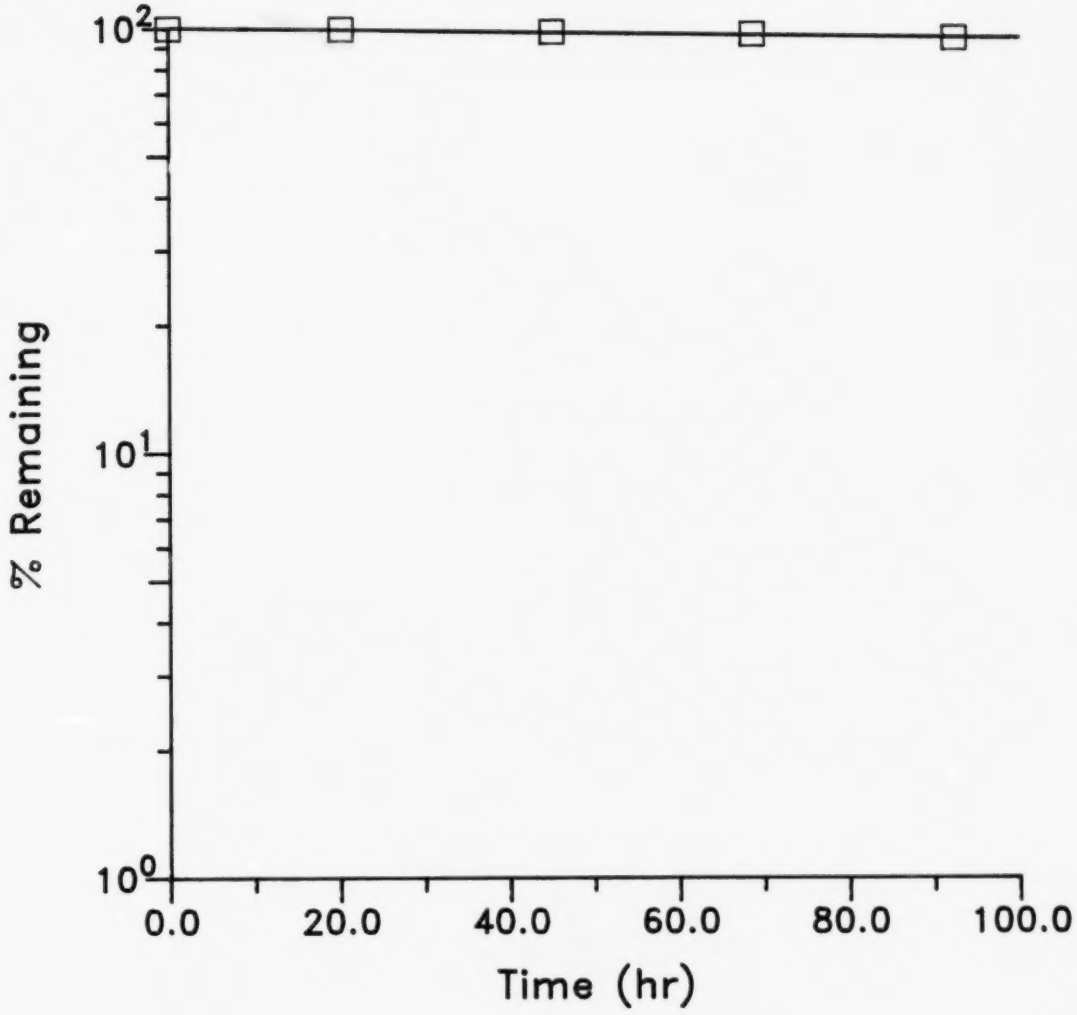


Figure 5.3.4 Hydrolysis of Brucine at 87°C, pH 7.16

5.3.4 Dieldrin
CAS No. 60-57-1

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^2K_1(d^{-1})$	$K_2(M^{-1}d^{-1})$	$t_{1/2}(d)$	r^2
3.13	69.0	3.6[a]		19.5	0.884
3.13	69.0	2.3		29.7	0.762
3.09	69.0	3.8		18.7	0.673
3.18	69.0	4.6		15.1	0.635
2.88	72.5	2.8		24.3	0.669
7.01	68.0	1.8		38.7	0.534
7.22	69.0	5.9		11.6	0.963
7.22	69.0	1.8		39.5	0.980
7.10	69.0	4.0		17.4	0.589
7.18	69.0	1.6		42.7	0.952
7.24	72.5	4.4		15.9	0.796
10.16	69.0	3.8		18.3	0.705
10.45	69.0	2.4		29.2	0.951
10.47	69.0	2.9		24.0	0.605
10.65	69.0	2.0		35.3	0.784
10.16	69.0	2.2		30.9	0.988
10.51	72.5	1.3		54.2	0.969

[a] Note units of K_1 are d^{-1}.

Water Solubility: 0.1 mg/l

Source: RTP Repository

Listed Purity: 99%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 10 ppb or 50 ppb

Analytical Procedure: The hydrolysis sample (10 ml) is extracted with 2 ml of iso-octane containing 100 ppb of aldrin. The extract is diluted 1:5 with iso-octane and analyzed by GC.

Extraction Solvent: Iso-octane 100 ppb aldrin

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

5.3.4 Dieldrin (Continued)

Detector: EC

Column: 30 M DB-5 0.25 micron film, 0.32 mm ID

Temperature Program: 200°C Iso

Mobile Phase: N/A

Internal Standard: Aldrin

Linear Range of Analysis:

5.3.4 Dieldrin

$K_1 = 2.5 \times 10^{-3}\ hr^{-1}$
$T_{1/2} = 11.6$ days
$R^2 = 0.963$

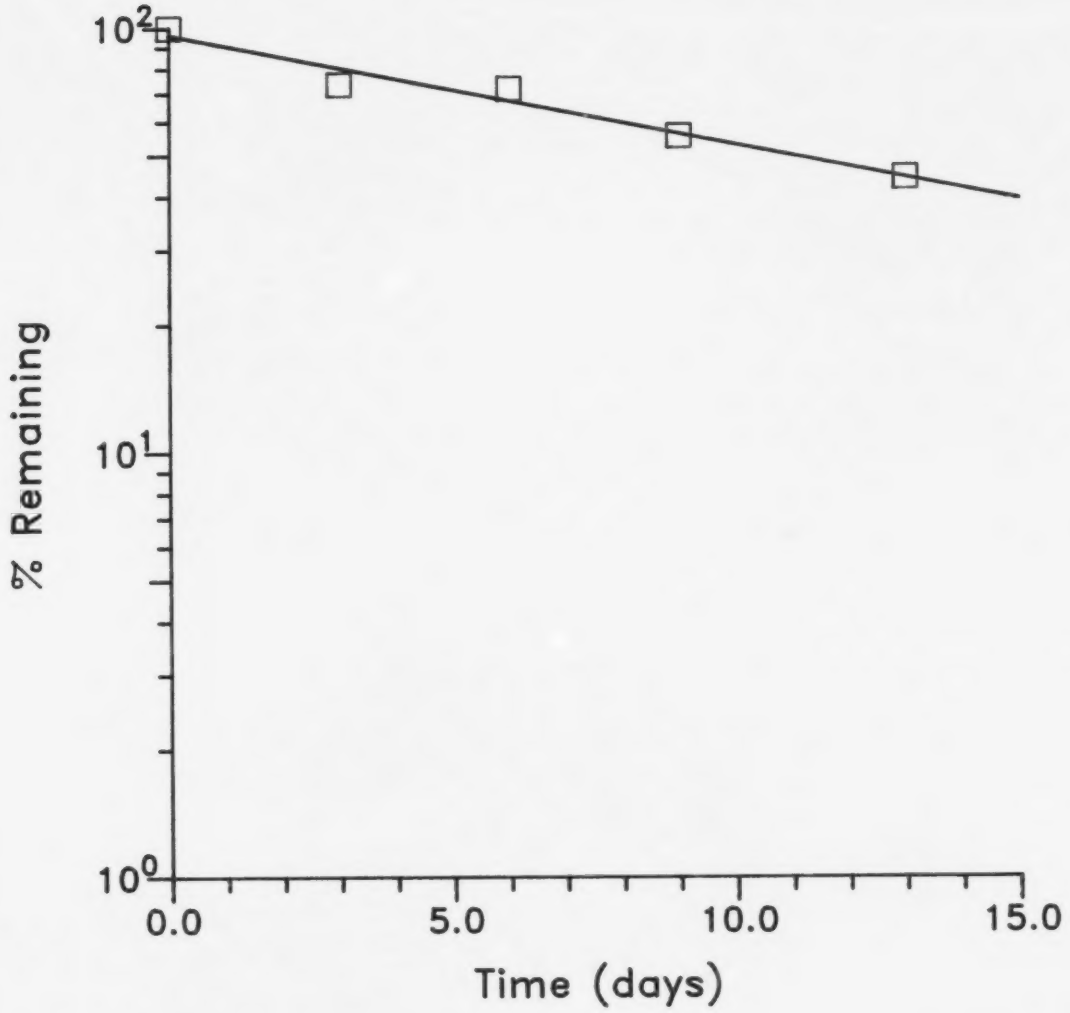


Figure 5.3.4 Hydrolysis of Dieldrin at 69°C, pH 7.22

5.3.5 Disulfoton
CAS No. 298-04-4

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^2K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.03	69.0	4.8		0.60	0.989
3.08	69.0	4.0		0.72	0.998
3.07	69.0	4.0		0.72	0.994
6.99	69.0	4.8		0.61	0.989
6.97	69.0	4.0		0.71	0.919
6.96	69.0	4.0		0.73	0.995
11	48.0	24.0	50.2	0.12	0.994
10.5	64.5	71.0	191	0.04	0.978
10.3	64.5	45.0	192	0.06	0.993

Comments: Activation energy calculated for alkaline hydrolysis was E_a = 17.5±1.3 K_{cal}/mole and Log A = 13.64±0.27, and K_2 = 5.99 $M^{-1}hr^{-1}$ at 25°C.

Water Solubility:

Source: RTP Repository

Listed Purity: 98.9%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 0.25 ppm

Analytical Procedure: At the time of analysis 10 ml of the buffered solution of disulfoton is extracted with 2 ml of iso-octane that contained chloropyrifos at 1.25 ppm. The iso-octane was diluted 1:5 to yield final concentrations 0.25 ppm disulfoton and 0.42 ppm chloropyrifos.

Extraction Solvent: iso-octane

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: Nitrogen-phosphorus

Column: 5M, OV-1, 2.65 micron film

Temperature Program: 185°C isothermal

Mobile Phase:

Internal Standard: Chloropyrifos (1.25 ppm in iso-octane)

5.3.5 Disulfoton

$K_1 = 0.24\ hr^{-1}$
$T_{1/2} = 2.8\ hr$
$R^2 = 0.994$

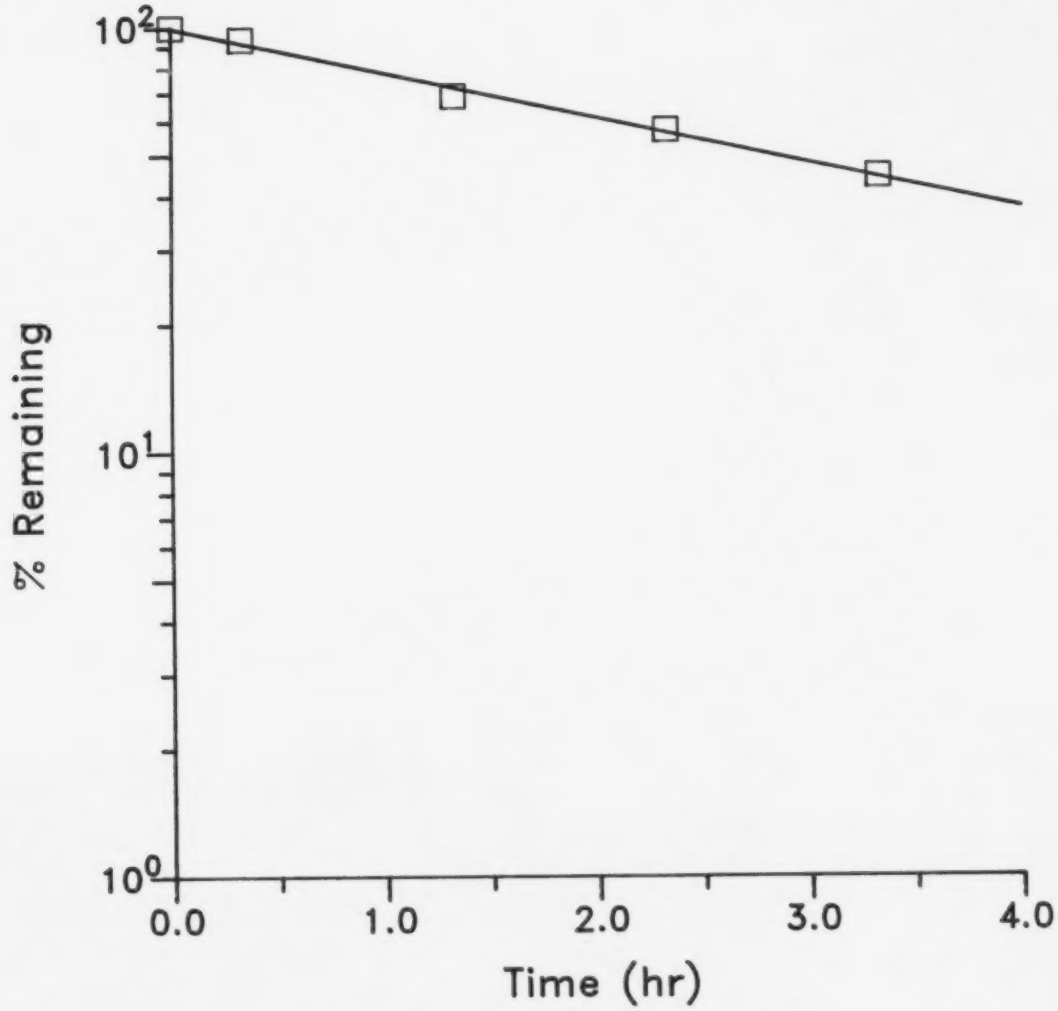


Figure 5.3.5 Hydrolysis of Disulfoton at 48°C, pH 11.00

5.3.6 Endosulfan I[1]
CAS No. 115-29-7

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^3K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.12	87.0	6.7	8.8	4.3	.951
3.24	87.0	5.8	10.1	5.0	.924
3.23	87.0	6.9	11.7	4.2	.801
6.89	68.0	300		0.10	.995
7.22	69.5	570		0.05	.977
7.23	69.5	580		0.05	.978
8.69	38.0	360	29,000	0.08	.984
8.89	38.0	1200	60,000	0.02	.961
9.05	38.0	1300	45,000	0.02	.990

Water Solubility: 0.53 mg/L

Source: RTP Repository

Listed Purity: 100%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 10 ppb

Analytical Procedure: Tubes containing 10 ml Endosulfan I or II, at the desired buffered pH (3, 7, or 11), were heated at a predetermined temperature. Tubes were sacrificed and the contents extracted with 1 ml iso-octane that contained 100 ppb Aldrin (internal standard). Dilution with iso-octane gave final concentrations of 10 ppb each Endosulfan and Aldrin.

Extraction Solvent: Iso-octane

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: EC

Column: DB-5, 15M, 0.25 micron film 0.32 mm ID

---

[1] OSW CAS No. 115-29-7 refers to Thiodan a mixture of Endosulfan I and Endosulfan II.

5.3.6 Endosulfan I[1] (Continued)

Temperature Program: 170°C - 220°C at 25°/min

Mobile Phase:

Internal Standard: Aldrin (100 ppb in iso-octane)

Linear Range of Analysis:

5.3.6 Endosulfan I

K_1 = 0.58 hr^{-1}
$T_{1/2}$ = 0.05 days
R^2 = 0.978

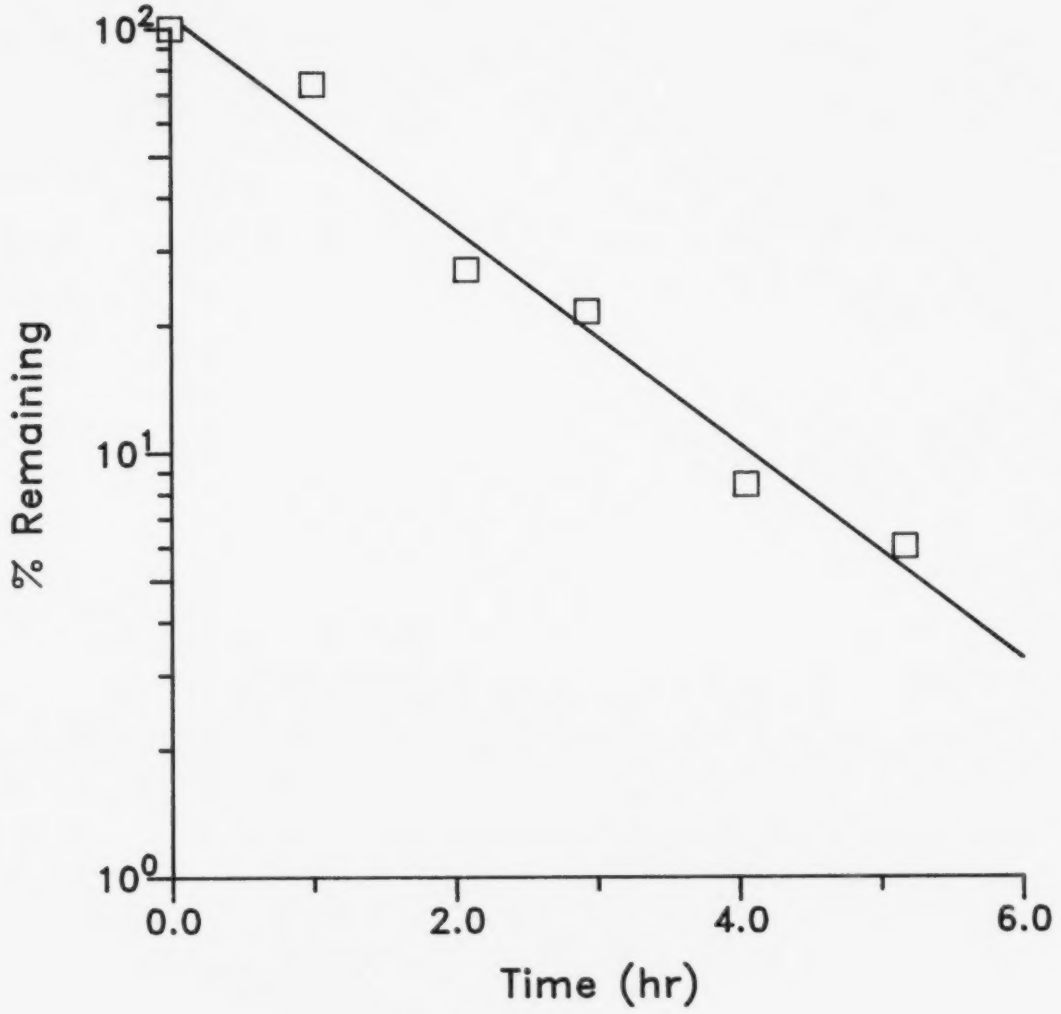


Figure 5.3.6 Hydrolysis of Endosulfan I at 69.5°C, pH 7.23

5.3.7 Endosulfan II[2]
CAS No. 115-29-7

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^3K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.40	87.0	7	17.5	4.1	0.579
3.33	87.0	10	21.4	2.9	0.970
3.32	87.0	11	23.0	2.7	0.980
6.89	68.0	400		0.07	0.997
7.24	69.5	670		0.04	0.975
7.23	69.5	740		0.04	0.964
8.69	38.0	680	$5.4x10^4$	0.04	0.993
8.82	38.0	1480	$8.7x10^4$	0.02	0.854
8.81	38.0	1110	$6.7x10^4$	0.03	0.800

Water Solubility: 0.28 mg/L

Source: RTP Repository

Listed Purity: 100%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 10 ppb

Analytical Procedure: Same as Endosulfan I

Extraction Solvent:

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: EC

Column: DB 5, 15M, 0.25 micron film, 0.32 mm ID

Temperature Program:

Mobile Phase:

Internal Standard:

Linear Range of Analysis:

---

[1] OSW CAS No. 115-29-7 refers to Thiodan a mixture of Endosulfan I and II.

5.3.7 Endosulfan II

K_1 = 0.68 hr^{-1}
$T_{1/2}$ = 0.04 days
R^2 = 0.993

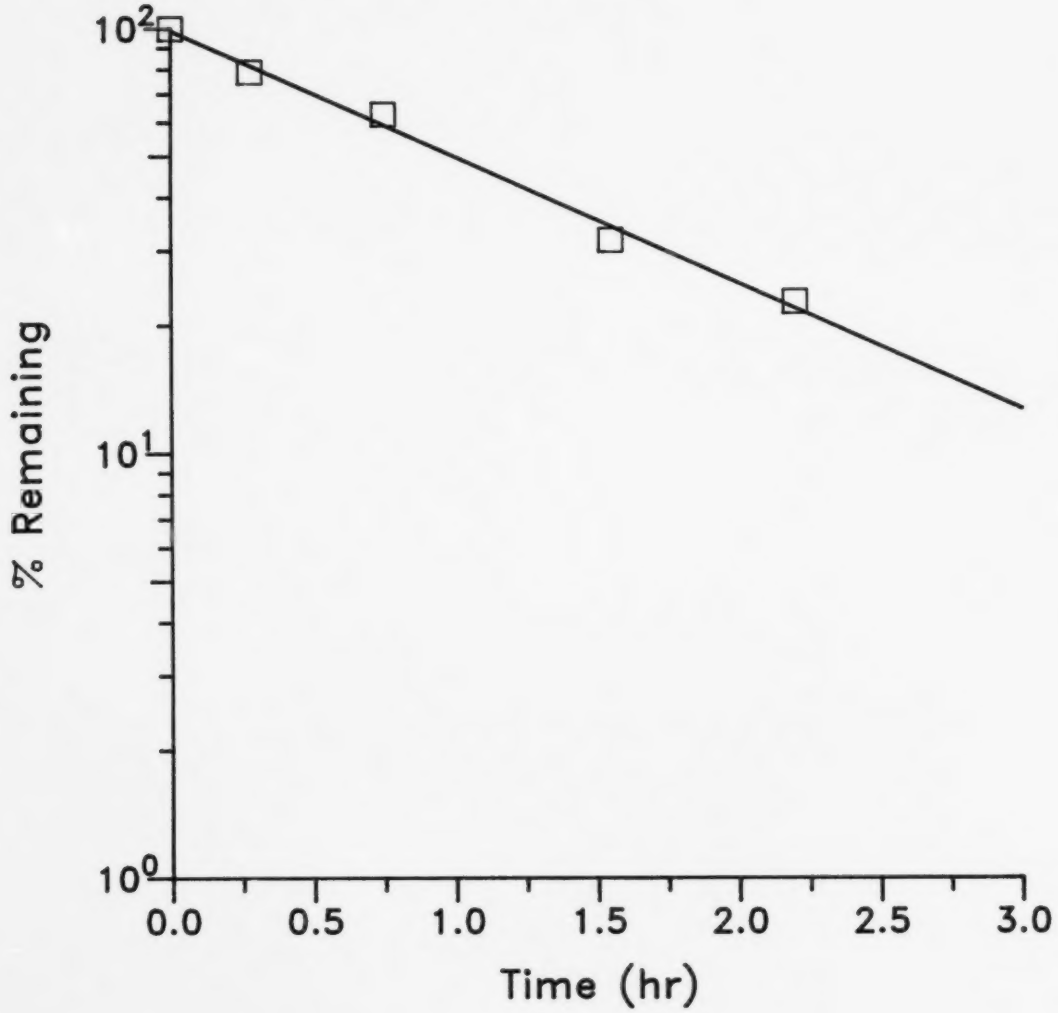


Figure 5.3.7 Hydrolysis of Endosulfan II at 38°C, pH 8.69

5.3.8 Fluoroacetic Acid, Sodium Salt
CAS No. 62-74-8

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^4 K_1 (hr^{-1})$	$K_2 (M^{-1}hr^{-1})$	$t_{1/2}$(d)	r^2
3.14	87.0	2.4		120	0.425
7.25	68.7	4.0		72	0.915
9.99	68.7	0.8		365	0.395

Comment: The pKa of fluoroacetic acid is 2.66. Thus, the rate constant at pH 3.14 includes hydrolysis contributions of the associated and disassociated species. Over most environmental conditions hydrolysis occurs in media >pH 4, thus the neutral and alkaline constants were used to determine $t_{1/2}$ at pH 7.

Water Solubility: Freely soluble

Source: RTP Repository

Listed Purity: 100%

Identity-Purity by Spectral Analysis:

Analysis Concentration: 4.8 ppm

Analytical Procedure: The analysis consisted of direct injection of 100 microliters directly onto the anion exchange column. Quantitation was by peak height comparison to the initial time zero height.

Extraction Solvent: NA

Instrumentation: GC ___ HPLC ___ IC _X_ Diode Array UV ___

Detector: Conductivity

Column: AS-3 Dionex Anion Column

Temperature Program: NA

Mobile Phase: 0.0025 M Sodium Carbonate, 0.003 M Sodium Bicarbonate

Internal Standard: NA

Linear Range of Analysis: 0.2 - 7.7 ppm

5.3.9 2-Methyllactonitrile
CAS No. 75-86-5

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$K_1(hr^{-1})$	$K_2(M^{-1}\ ^{-1})$	$t_{1/2}(d)$	r^2
7.02	26.0	4.47		$6.5x10^{-3}$	.976

Comment: This is an equilibrium reaction between acetone and hydrogen cyanide to form a cyanohydrin.

Water Solubility: Dissociates

Source: Aldrich

Listed Purity: 99%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 1.5 ppm

Analytical Procedure: Direct analysis on UV after use of modified EPA Wastewater Procedure 335 (Barbituric Acid/Pyridine/Chloramine T method) detects HCN formed by hydrolysis of compound of interest.

Extraction Solvent: NA

Instrumentation: GC ___ HPLC ___ IC ___ Diode Array UV X

Detector: UV at 578 nm

Column: NA

Temperature Program: NA

Mobile Phase: NA

Internal Standard: NA

Linear Range of Analysis: 0.02 ppm - 10 ppm (as CN^-)

5.3.10 Nitroglycerine
CAS No. 55-63-0

HYDROLYSIS AND ANALYSIS DATA

Literature Data[a]:

Temp, °C	$10^2 K_b (M^{-1} sec^{-1})$
25	2.36
25	1.94
18	0.83
18	0.61
10	0.22
10	0.15
10	0.12

[a] Capellos, C., et al., Int. J. Chem. Kinet. 16, 1027-1051 (1984).

Authors reported activation energy as 27.53 Kcal/mole

Water Solubility: 1800 mg/l

Source:

Listed Purity:

Identity-Purity by Spectral Analysis:

Analysis Concentration:

Analytical Procedure: See Ref. 1 in Section 1.3.

Extraction Solvent:

Instrumentation: GC ___ HPLC ___ IC ___ Diode Array UV ___

Detector:

Column:

Temperature Program:

Mobile Phase:

Internal Standard:

Linear Range of Analysis:

5.3.11 Famphur
CAS No. 52-85-7

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^2K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.09	68.0	1.4		2.1	0.722
3.09	69.0	4.7		0.61	0.993
3.03	69.0	4.7		0.62	0.985
6.99	68.0	4.7		0.61	0.926
7.01	69.0	3.0		0.95	0.865
7.02	69.0	5.0		0.57	0.928
11.0	48.0	42	88.0	0.07	0.989
10.38	69.0	297	858	0.010	0.994
10.39	69.0	303	854	0.009	0.999

Comments: Calculated alkaline E_a = 23.6±1.0 K_{cal}/mole, log A = 18.1±0.3 and K_2 = 5.0 $M^{-1}hr^{-1}$ at 25°C.

Water Solubility:

Source: RTP Repository

Listed Purity: 98.1%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 0.53 ppm

Analytical Procedure: At the time of analysis 10 ml of a buffer solution of famphur is extracted with 2 ml of iso-octane that contains chloropyrifos IS. Dilutions before analyses yield a chloropyrifos concentration of 0.42 ppm.

Extraction Solvent: Iso-octane

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: Nitrogen-phosphorus

Column: OV-1, 5M, 2.65 micron film, 0.53 mm ID

Temperature Program: 185° Isothermal

Mobile Phase: NA

Internal Standard: Chloropyrifos (0.42 ppm in iso-octane)

5.3.11 Famphur

K_1 = 3.03 hr^{-1}
$T_{1/2}$ = 0.01 days
R^2 = 0.999

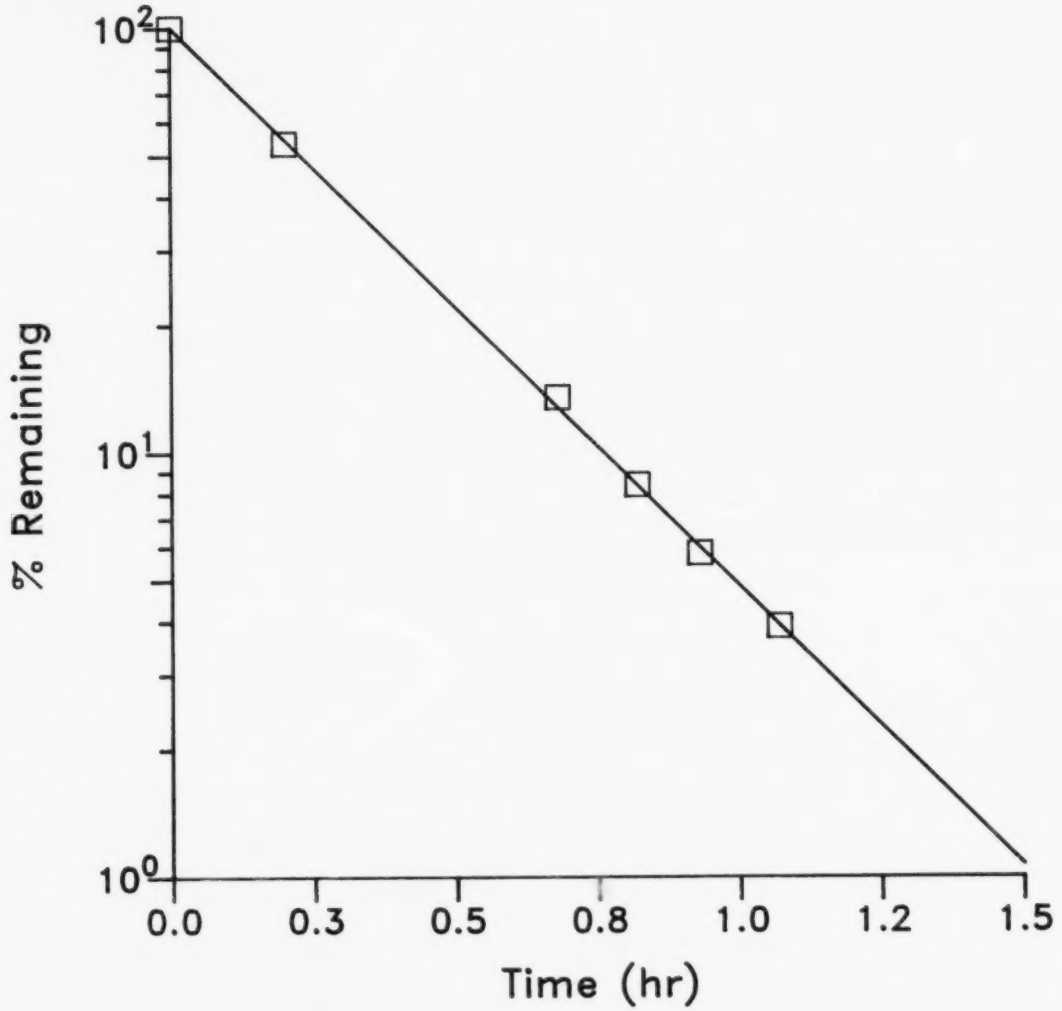


Figure 5.3.11 Hydrolysis of Famphur at 69.5°C, pH 10.79

5.3.12 Acrylamide
CAS No. 79-06-1

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data: pH	Temp, °C	$10^4 K_1 (hr^{-1})$	$K_2 (M^{-1}hr^{-1})$	$t_{1/2}$(d)	r^2
2.99	88.0	17		0.9	0.389
2.99	88.0	<125	<4.6	2.3	0.890
7.04	88.0	3.0		96.3	0.017
7.04	88.0	26		11.1	0.470
7.04	88.0	49		6.0	0.925

11.54 (See comments)

Comments: Samples at pH 11.54 became cloudy followed by the appearance of globules. Less than 10% of the acrylamide disappeared during the time of the hydrolysis experiment at acid and neutral pH, this contributed to the scatter in the data.

Water Solubility: 2050 g/l

Source: Chem. Serv.

Listed Purity: Unknown

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 2 ppm

Analytical Procedure: Direct aqueous injections of on microliter aliquots were made on column. Ethyl carbamate was added to each tube before analysis.

Extraction Solvent: NA

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: FID

Column: DB Wax+, 30 m, 1 micron film, 0.53 mm ID

Temperature Program: 95°C to 190°C

Mobile Phase: NA

Internal Standard: Ethyl carbamate at 8 ppm

5.3.13 Acrylonitrile
CAS No. 107-13-1

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^4K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
2.87	68.0	64		4.5	0.811
2.87	68.0	71		4.1	0.533
7.19	68.0				
7.19	68.0	No measurable disappearance after two days			
7.19	68.0				
10.76	68.6	4000	48.1	0.07	0.991
11.76	68.6	9100	109.4	0.03	0.964
10.76	68.2	8900	109.3	0.03	0.977

Comments: The failure to observe hydrolysis is consistent with the reported hydrolysis pathways for nitriles, and with J. Going (1978) Environmental Monitoring Near Industrial Sites: Acrylonitrile, EPA 560/6-79-003 (PB 295-928). Going reported zero degradation after 23 days at room temperature and at three levels of pH (4, 7, and 10).

Water Solubility: 73.5 g/l

Source: Aldrich

Listed Purity: +99%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 5.79 ppm

Analytical Procedure: Keep light from solutions of acrylonitrile to prevent polymerization. One microliter aliquots of the buffer solution were injected onto a DB Wax+ capillary column. A one meter section of blank tubing was placed between the injection port and inlet end on the column to trap the buffer salts.

Extraction Solvent: NA

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: FID

Column: DB Wax+, 30M, 1 micron film, 0.53 mm ID

5.3.13 Acrylonitrile (Continued)

Temperature Program: 30°C isothermal

Mobile Phase: NA

Internal Standard: Propionitrile at 6 ppm

Linear Range of Analysis:

5.3.14 Mitomycin C
CAS No. 50-07-7

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^2K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
7.54	68.7	1.7		1.7	0.999
9.25	69.0	9.6	350	0.3	0.987
9.42	69.0	19.0	477	0.15	0.992
8.64	69.0	3.9	590	0.74	0.984

Literature data:[a,b]

pH	Temp, °C	$10^5K_1(sec^{-1})$	$K_1(hr^{-1})$	$t_{1/2}(d)$
2.1	25	135.0	4.86	0.006
3.2	25	46.0	1.66	0.017
3.3	25	19.0	0.68	0.042
3.6	25	15.6	0.56	0.052
3.9	25	11.5	0.41	0.070
4.3	25	3.3	0.12	0.24

Extrapolation of the literature data to pH 7 gave a half-life of 18 days at 38°C.

---

[a] McClelland, R. A. and K. Lam. 1985. Kinetics and Mechanism of the Acid Hydrolysis of Mitomycin. J. Am. Chem. Soc. 107, 5182-5186.

[b] Beijnen, J.H., et al. J. Pharm. Biomed. Anal. 3, 59-69 (1985).

Water Solubility:

Source: Aldrich

Listed Purity:

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 1 ppm

Analytical Procedure: The Mitomycin C is sold as 2 mg sorbed to 48 mg sodium chloride. A stock solution was prepared by dissolving total contents of package in 5 ml of HPLC mobile phase. Dilution of stock solution with buffers gave the final solutions for hydrolysis determinations.

Extraction Solvent: NA

5.3.14 Mitomycin C (Continued)

Instrumentation: GC ___ HPLC X IC ___ Diode Array UV ___

Detector: UV at 360 nm

Column: u Bondapak C18, 4.6 mm x 30 cm

Temperature Program:

Mobile Phase: Methanol/0.05 M KH_2PO_4, pH 7 (35:65)

Internal Standard: None

Linear Range of Analysis: 0.055 - 1.1 ppm

5.3.14 Mitomycin C

$K_1 = 1.7 \times 10^{-2}\ hr^{-1}$
$T_{1/2} = 40.7\ hr$
$R^2 = 0.999$

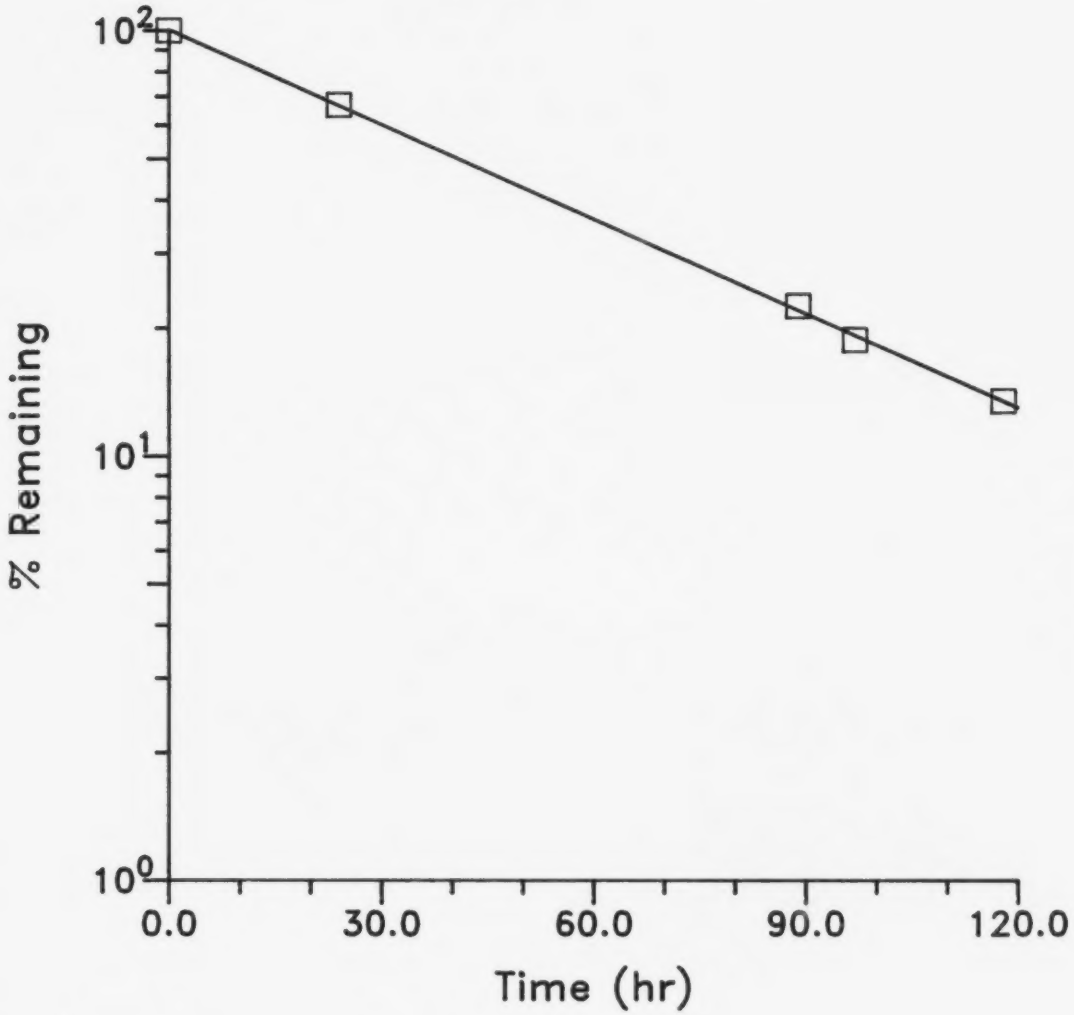


Figure 5.3.14 Hydrolysis of Mitomycin C at 68.7°C, pH 7.54

5.3.15 Chloromethyl Methyl Ether
CAS No. 107-30-2

HYDROLYSIS AND ANALYSIS DATA

Literature Data[a]: Reference 2 in Section 1.3
$k_h = 21\ hr^{-1}$ $T_{1/2} = 1.99$ min

---

[a] Van Duuren, B.L., et al. J. Natl. Cancer Inst. 48(5) 1431-1439 (1972).

Water Solubility:

Source:

Listed Purity:

Identity-Purity by Spectral Analysis:

Analysis Concentration:

Analytical Procedure: See ref. 2 in Section 1.3

Extraction Solvent:

Instrumentation: GC ___ HPLC ___ IC ___ Diode Array UV ___

Detector:

Column:

Temperature Program:

Mobile Phase:

Internal Standard:

Linear Range of Analysis:

5.3.16 1,2-Dibromo-3-Chlioropropane (DBCP)
CAS No. 92-12-8

HYDROLYSIS AND ANALYSIS DATA

Literature Data[a]:

Literature Values: The kinetic data for hydrolysis of DBCP suggests a rate law that is first order in DBCP and first order in hydroxide down to pH 7. Below pH 7 the rate depends in part on hydrolysis by water. The energy of activation for the pH 6.8 Arrhenius plut was 22.34 Kcal/mole.

K_{OH} = 20.6 $M^{-1}hr^{-1}$ (At 25°C and pH 7 data predict a half-life of 38 ± 4 years)

---

[a] Burlinson, N. E., L. A. Lee, and D. H. Rosenblatt. 1982. Kinetics and Products of Hydrolysis of 1,2-Dibromo-3-Chloropropane. Environ. Sci. Technol. 16, 627-632.

Water Solubility: 1 g/l

Source:

Listed Purity:

Identity-Purity by Spectral Analysis:

Analysis Concentration:

Analytical Procedure: See ref. 4, Section 1.3

Extraction Solvent:

Instrumentation: GC ___ HPLC ___ IC ___ Diode Array UV ___

Detector:

Column:

Temperature Program:

Mobile Phase:

Internal Standard:

Linear Range of Analysis:

5.3.17 Ethylene Dibromide
CAS No. 106-93-4

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data[a]:

pH	Temp, °C	No. of Sample Points	$10^4 K_1 (hr^{-1})$	$t_{1/2}$(d)	r^2
5	30	38	1.6 (17%)	180	0.475
5	45	69	10	29	0.916
5	60	59	32	9	0.946
7	30	51	0.7	410	0.460
7	45	66	5.0	57	0.717
7	60	63	26.9	11	0.975
9	30	56	1.7	170	0.582
9	45	66	10.6	28	0.963
9	60	65	42.2	6.9	0.991

The activation energies determined from the slopes of pH 5, 7, and 9 plots were 19.9, 24.1, and 21.1 Kcal/deg-mole, respectively. At pH 7, the hydrolysis half-life extrapolated from the data to 20°C is 15 years.

1. % Relative standard deviation

---

[a] Cohen, S. Z. (Office of Pesticides, EPA) and G. A. Jungclaus (Midwest Research Institue). Hydrolysis of Ethylene dibromide, Manuscript in review.

Water Solubility:

Source:

Listed Purity:

Identity-Purity by Spectral Analysis:

Analysis Concentration:

Analytical Procedure: See ref. 3, Section 1.3.

Extraction Solvent:

Instrumentation: GC ___ HPLC ___ IC ___ Diode Array UV ___

5.3.17 Ethylene Dibromide (Continued)

Detector:

Column:

Temperature Program:

Mobile Phase:

Internal Standard:

Linear Range of Analysis:

5.3.18 cis-1,4-Dichloro-2-butene
CAS No. Reference 764-41-0[1]

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(hr)$[a]	r^2
2.98	68.0	1.09		0.64	0.994
3.04	69.0	1.37		0.51	0.990
3.12	69.0	1.34		0.52	0.984
7.04	68.0	1.07		0.65	0.998
7.16	69.0	1.33		0.52	0.993
7.18	69.0	1.40		0.50	0.990
6.99	57.0	0.50		1.38	0.966
7.00	57.0	0.47		1.43	0.997
9.74	69.0	1.40		0.50	0.998
9.96	69.0	1.26		0.55	0.964
10.62	68.0	1.46		0.47	0.999

[a] Note $t_{1/2}$ unit is hr.

Water Solubility:

Source: Aldrich

Listed Purity: cis purity = 95%, trans purity = 85%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 0.27 ppm

Analytical Procedure: Ten (10) ml of hydrolysis solution was extracted with 2 ml of 14.4 ppm 1,2,3-trichloropropane in iso-octane. The extract was diluted 1:50 before analysis.

Extraction Solvent: Iso-octane

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

---

1 CAS No. for trans isomer is 110-57-6.

5.3.18 cis-1,4-Dichloro-2-butene (Continued)

Detector: EC

Column: OV-1, 5 M, 2.65 micron film, 0.53 mm ID

Temperature Program: 45°C isothermal

Mobile Phase: NA

Internal Standard: 1,2,3-Trichloropropane (14.4 ppm in iso-octane)

Linear Range of Analysis:

5.3.18 cis-1,4-Dichloro-2-butene

K_1 = 1.33 hr^{-1}
$T_{1/2}$ = 0.02 days
R^2 = 0.993

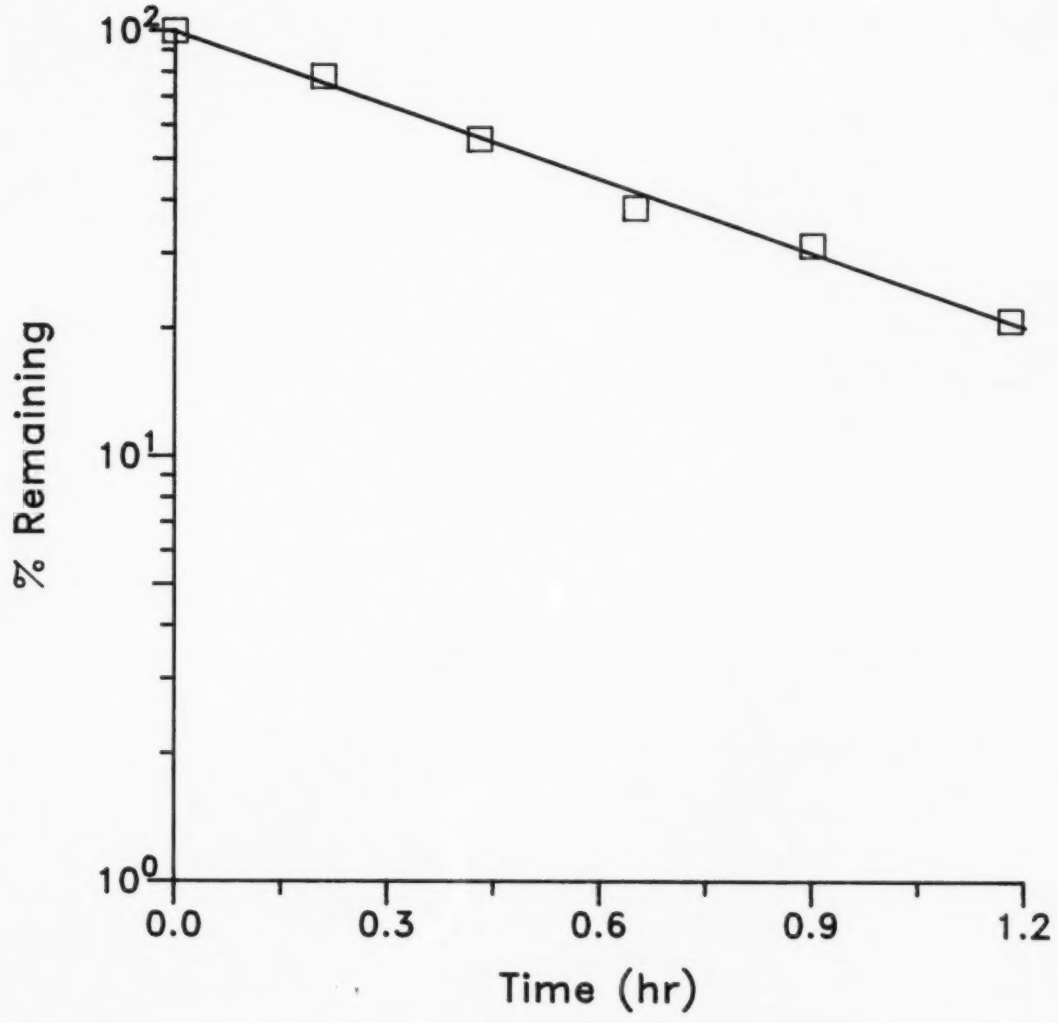


Figure 5.3.18 Hydrolysis of cis-1,4-Dichloro-2-butene at 69°C, pH 7.16

5.3.19 trans-1,4-Dichloro-2-butene
CAS No. Reference 110-57-6

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(hr)$[a]	r^2
2.96	68.0	1.47		0.47	0.996
3.02	69.0	1.28		0.54	0.997
3.00	69.0	1.36		0.51	0.996
7.01	68.0	1.30		0.53	0.970
7.03	69.0	1.42		0.49	0.998
7.03	69.0	1.33		0.52	0.998
10.51	68.0	1.30		0.54	0.999
9.90	69.0	1.49		0.47	0.993
9.90	69.0	1.45		0.48	0.999

[a] Note $t_{1/2}$ unit is hr.

Water Solubility:

Source: Aldrich

Listed Purity: 85%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 0.27 ppm

Analytical Procedure: See 5.3.18

Extraction Solvent: Iso-octane

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: EC

Column: OV-1, 5M, 2.65 micron film, 0.53 mm ID

5.3.19 trans-1,4-Dichloro-2-butene (Continued)

Temperature Program: 45°C Isothermal

Mobile Phase:

Internal Standard: 1,2,3-Trichloropropane (14.4 ppm in iso-octane)

Linear Range of Analysis:

5.3.19 trans-1,4-Dichloro-2-butene

K_1 = 1.45 hr^{-1}
$T_{1/2}$ = 0.02 days
R^2 = 0.999

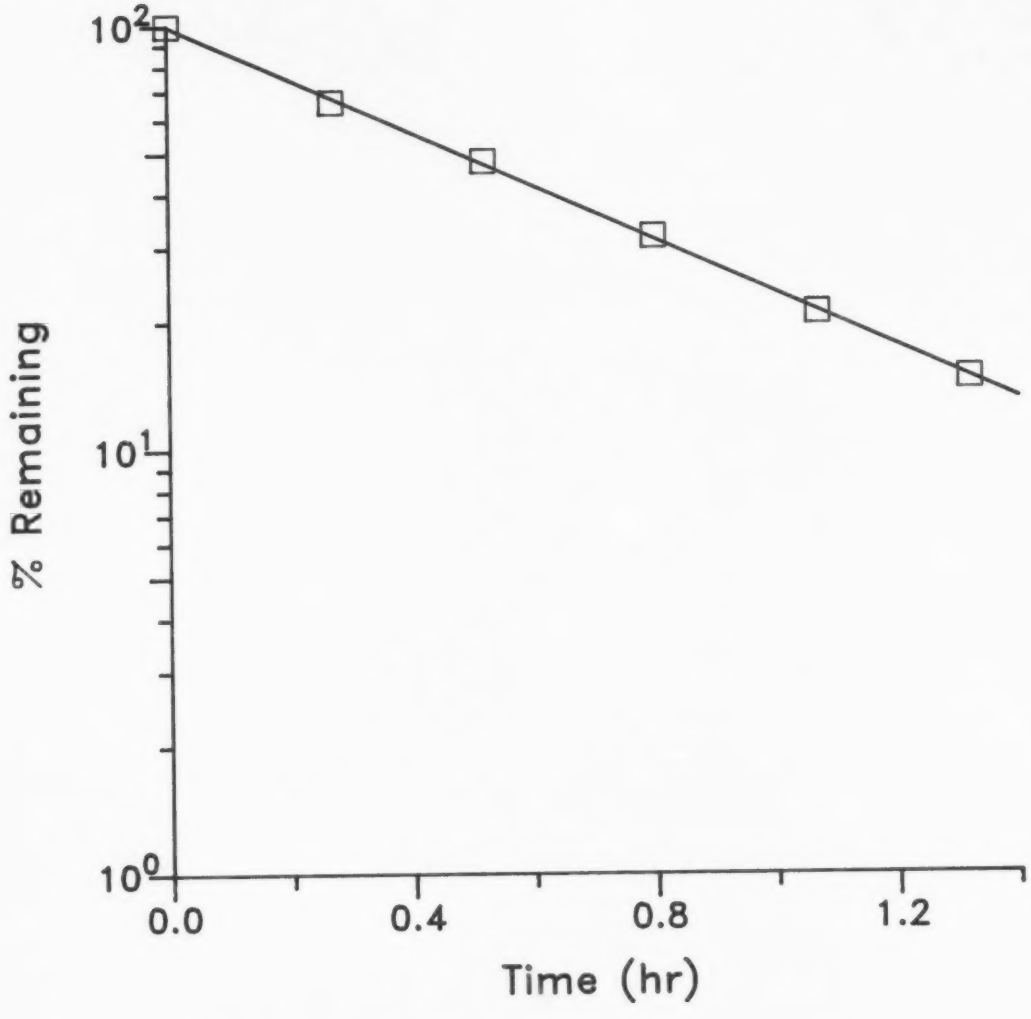


Figure 5.3.19 Hydrolysis of trans-1,4-Dichloro-2-butene at 69°C, pH 9.90

5.3.20 4,4-Methylene-bis-(2-Chloroaniline)
CAS No. 101-14-4

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^4K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.10	87.0	5.4		51	0.928
3.10	87.0	3.5		83	0.993
3.10	87.0	2.2		131	0.702
7.62	87.0	<1.1		250	NA
9.78	87.0	<1.1		250	NA

Comment: Protonation of the amine at pH 3 may lead to enhanced hydrolysis of the chloro groups. The data at pH 7 and 9 are based on three runs at each pH with very limited reaction.

Water Solubility: 25 mg/l

Source: Pfaltz and Bauer

Listed Purity: 97%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 3.2 ppm

Analytical Procedure: Direct injection of 20 microliters with HPLC and UV or electrochemiccal detection. Diluted the tube contents 1:10 with mobile phase at the time of analysis. HPLC separation followed by UV or electrochemical detection.

Extraction Solvent: NA

Instrumentation: GC ___ HPLC X IC ___ Diode Array UV ___

Detector: Kratos 757, 248 nm or BAS Electrochemical 0.9V, 10 nA

Column: Zorbax ODS, 5 micron or Resolvex C18, 10 micron

Temperature Program:

Mobile Phase: 80% acetonitrile/20% water with Zorbax col.
50% acetonitrile/50% 0.05M KH_2PO_4 with Resolvex col.

5.3.20 4,4-Methylene-bis-(2-Chloroaniline) (Continued)

Internal Standard:

Linear Range of Analysis:

5.3.20 4,4'-Methylene-bis-(2-chloroaniline)

$K_1 = 5.6 \times 10^{-4}\ hr^{-1}$
$T_{1/2} = 51$ days
$R^2 = 0.928$

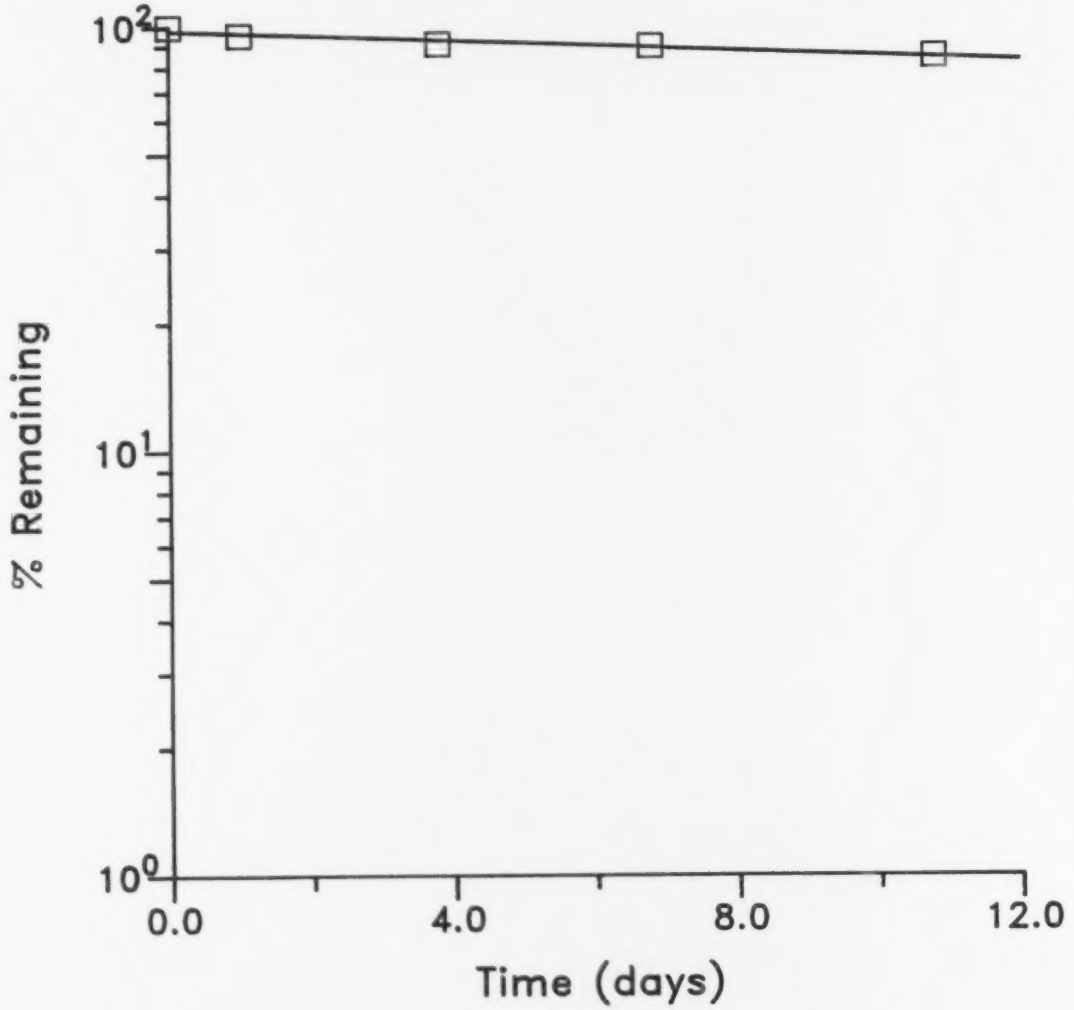


Figure 5.3.20 Hydrolysis of 4,4'-Methylene-bis -(2-chloroaniline) at 87°C, pH 3.1

5.3.21 Pentachloronitrobenzene
CAS No. 82-68-8

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^3K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.10	68.0	5.0		5.7	0.995
3.02	69.0	3.7		7.8	0.997
3.11	69.0	6.3		4.6	0.918
7.01	68.5	2.6		11	0.947
7.09	69.0	2.9		9.9	0.906
7.17	69.0	3.9		7.5	0.912
10.50	68.0	6.4		4.5	0.996
10.43	69.0	3.4		8.5	0.930
10.62	69.0	4.2		6.9	0.918

Water Solubility: 0.43 mg/L

Source: Aldrich

Listed Purity: 96%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 0.03 ppm

Analytical Procedure: Same as pronamide.

Extraction Solvent: iso-octane

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: EC

Column: DB-5, 30M, 0.25 micron film, 0.32 mm ID

Temperature Program: 140° isothermal

Mobile Phase:

Internal Standard: Methyl ester of 2,4-D (52.5 ppb in iso-octane)

Linear Range of Analysis:

5.3.21 Pentachloronitrobenzene

$K_1 = 2.6 \times 10^{-3}\ d^{-1}$
$T_{1/2} = 11$ days
$R^2 = 0.947$

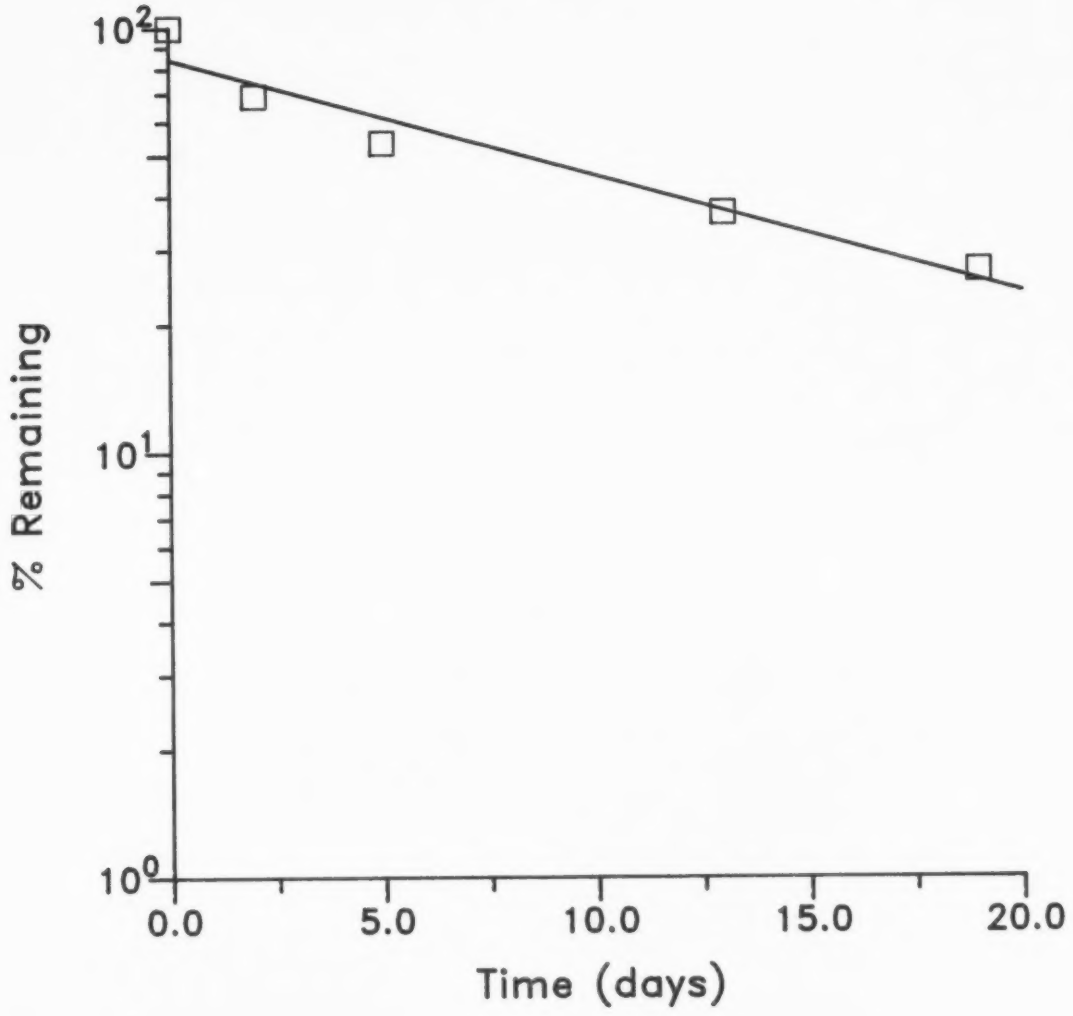


Figure 5.3.21 Hydrolysis of Pentachloronitrobenzene at 68.5°C, pH 7.01

5.3.22 Pronamide
CAS No. 23950-58-5

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^4 K_1 (hr^{-1})$	$K_2 (M^{-1}hr^{-1})$	$t_{1/2}$(d)	r^2
3.10	68.0	7.9	0.6	36.6	0.930
7.11	68.0	<2.1		>138	n/a
7.06	49.0	<2.1		>138	n/a
10.20	68.0	240.0	10.5	1.2	0.987

Comment: Neutral hydrolysis values were ignored in calculating half-life since contribution from neutral rate was neglible.

Water Solubility: 15 mg/L

Source: RTP Repository

Listed Purity: 98.7%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 0.1 ppm

Analytical Procedure: At the time for analysis of each tube, the buffered solution (10 ml) of pronamide (0.1 ppm) was extracted with 1 ml of iso-octane that contained 2,4-D methyl ester (5.25 ppm). The extract is diluted 1:100 with iso-octane to yield 10 ppb pronamide and 52.5 ppb 2,4-D methyl ester.

Extraction Solvent: iso-octane

Instrumentation: GC _X_ HPLC ___ IC ___ Diode Array UV ___

Detector: EC

Column: DB-5, 30M, 0.25 micron film, 0.32 mm ID

Temperature Program: 140°C isothermal

Mobile Phase:

Internal Standard: Methyl ester of 2,4-D (52.5 ppb in iso-octane)

Linear Range of Analysis: 1 - 10.1 ppb

5.3.22 Pronamide

$K_1 = 7.9 \times 10^{-4}\ hr^{-1}$
$T_{1/2} = 36.6$ days
$R^2 = 0.930$

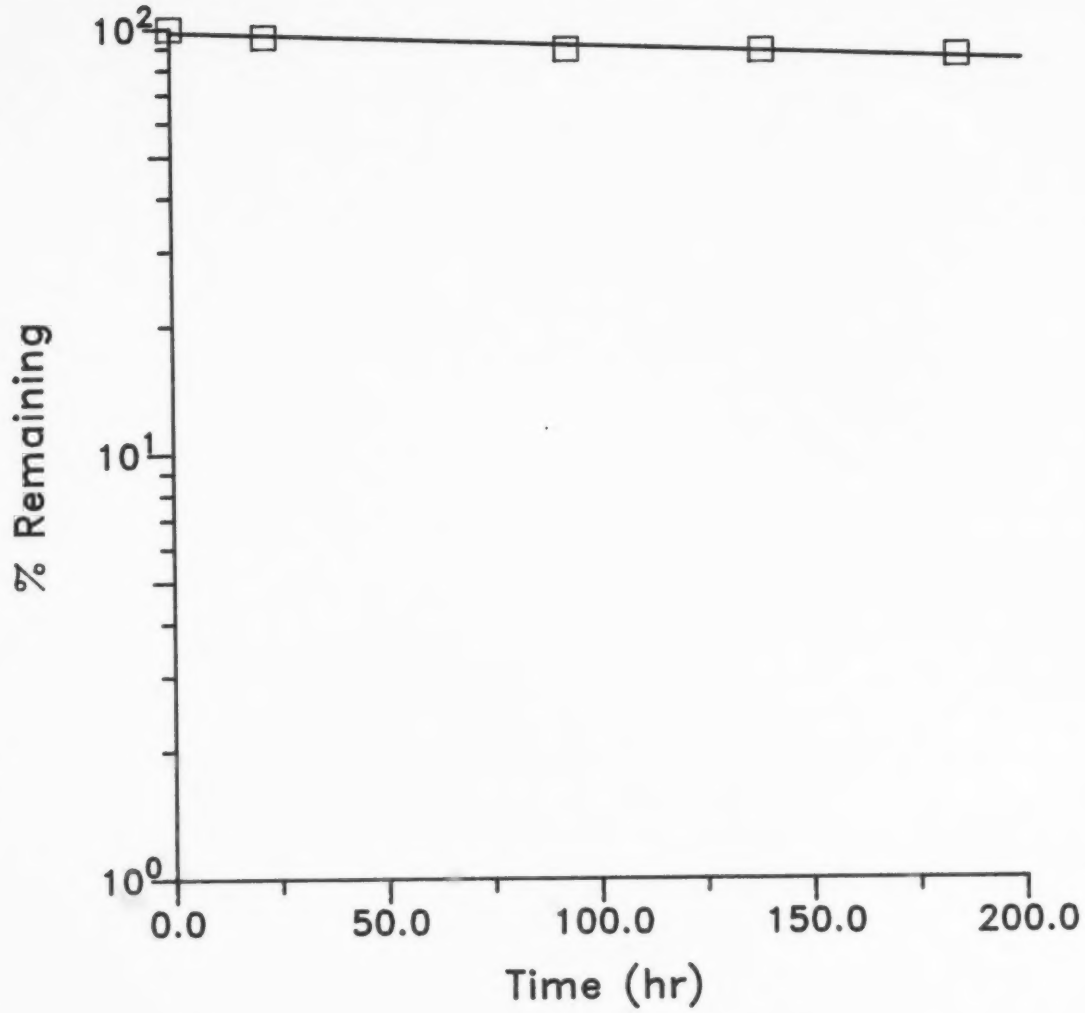


Figure 5.3.22 Hydrolysis of Pronamide at 68°C, pH 3.10

5.3.23 Reserpine
CAS No. 50-55-5

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data: pH	Temp, °C	$10^3K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.02	70.0	0.93	0.97	31.0	0.623
2.99	70.0	0.70	0.68	41.0	0.566
7.01	68.0	6.8		4.3	0.700
7.06	70.0	8.1		3.6	0.986
7.01	70.0	9.5		3.0	0.941
10.21	68.0	1810	773	0.016	0.991
10.02	70.0	2270	1375	0.013	0.995
9.79	70.0	1970	2016	0.015	0.976

Water Solubility:

Source: Aldrich

Listed Purity: 99%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 1.5 ppm

Analytical Procedure: At the time of analysis each tube at pH 3 or pH 11 is neutralized with 0.5M sodium biphosphate buffer. Twenty microliters of the neutralized solutions is then injected into the HPLC for analysis.

Extraction Solvent:

Instrumentation: GC ___ HPLC X IC ___ Diode Array UV ___

Detector: Kratos 757 UV, 216 nm

Column: Waters Nova-Pak C18, 15 cm x 4.6 mm, 5 micron

Temperature Program:

Mobile Phase: 50% acetonitrile, 5% 0.05M sodium diphosphate

Internal Standard:

Linear Range of Analysis:

5.3.23 Reserpine

$K_1 = 2.27\ hr^{-1}$
$T_{1/2} = 0.01$ days
$R^2 = 0.995$

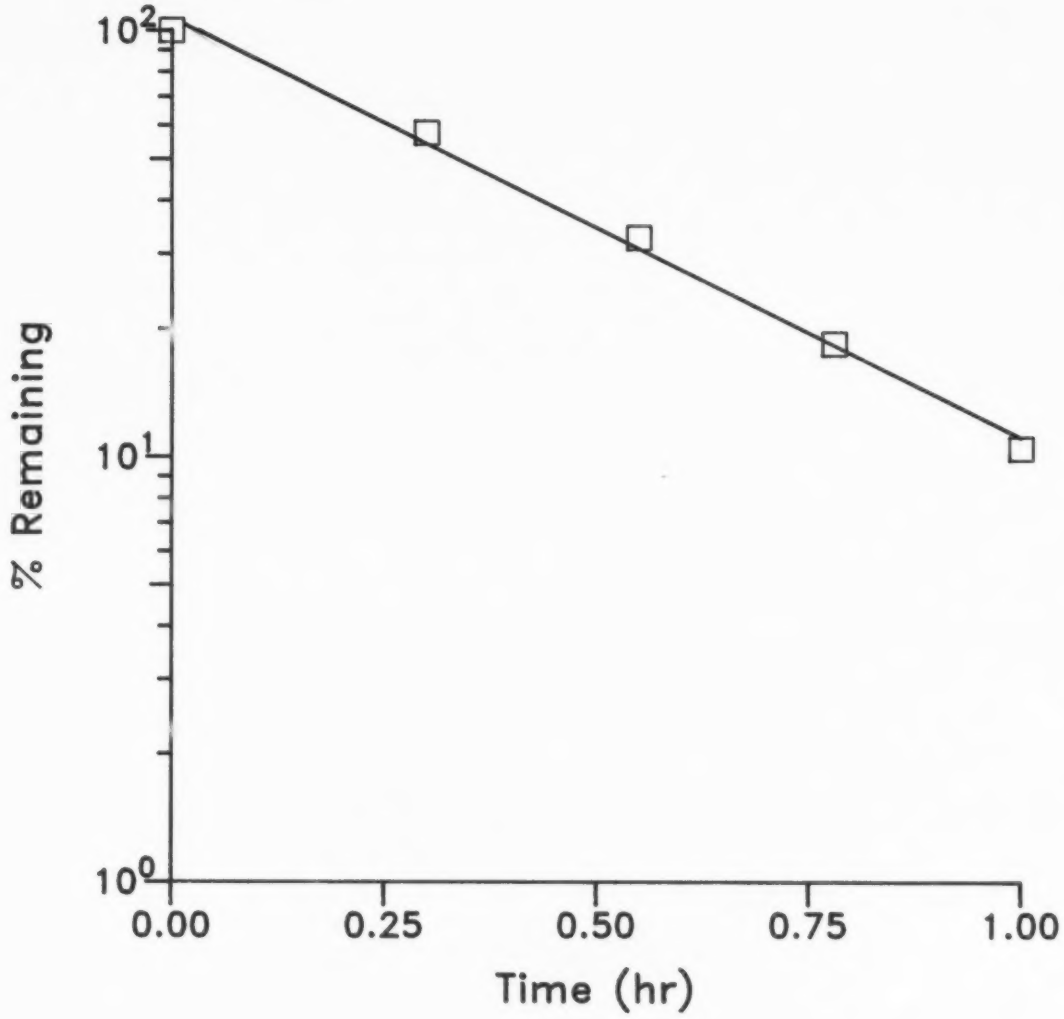


Figure 5.3.23 Hydrolysis of Reserpine at 70°C, pH 10.02

5.3.24 Thiourea
CAS No. 62-56-6

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data: Degradation was monitored at pH 3, 7, and 11 at 70° fr 6, 10, and 6 days, respectively. Zero degradation was observed.

Assuming 2% degradation over 10 days would give $K_1 = 2.02 \times 10^{-3} d^{-1}$ and $t_{1/2}$ = 300d at 70°C.

Water Solubility: 91.8 g/l

Source: Chem. Serv.

Listed Purity: Unknown

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 1.1

Analytical Procedure: Individual hydrolysis run tubes were sacrificed and the contents absorbance measured by scanning 200-270 nm referenced to the buffer blank. The diode array detector was used for the analysis.

Extraction Solvent: NA

Instrumentation: GC ___ HPLC ___ IC ___ Diode Array UV X

Detector: UV

Column: NA

Temperature Program: NA

Mobile Phase: NA

Internal Standard:

Linear Range of Analysis:

5.3.25 Uracil Mustard
CAS No. 66-75-1

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1}$	$t_{1/2}(d)$	r^2
5.04	22.2	0.35		0.08	0.999
5.07	31.7	1.16		0.025	0.999
5.08	31.7	1.09		0.027	0.996
7.03	22.2	0.40		0.072	0.996
7.08	31.7	1.38		0.021	0.999
7.31	31.7	1.53		0.019	0.997
9.00	22.2	2.13	2.09×10^5	0.014	0.999
9.04	23.0	2.13	2.09×10^5	0.014	0.994
9.01	23.0	2.02	1.98×10^5	0.014	0.997

Water Solubility:

Source: Upjohn Company

Listed Purity: Assumed 100%

Identity-Purity by Spectral Analysis:

Analysis Concentration: 5.2 ppm

Analytical Procedure: Direct injection of 20 microliter of the hydrolysis sample.

Extraction Solvent: NA

Instrumentation: GC ___ HPLC _X_ IC ___ Diode Array UV ___

Detector: UV 257

Column: Waters Nova-Pak C18 5 micron (15 cm x 4.6 mm)

Temperature Program: NA

Mobile Phase: 20% acetonitrile/80% water

Internal Standard:

Linear Range of Analysis: 0.21 - 10.5 ppm

5.3.25 Uracil Mustard

$K_1 = 0.40\ hr^{-1}$
$T_{1/2} = 0.07$ days
$R^2 = 0.996$

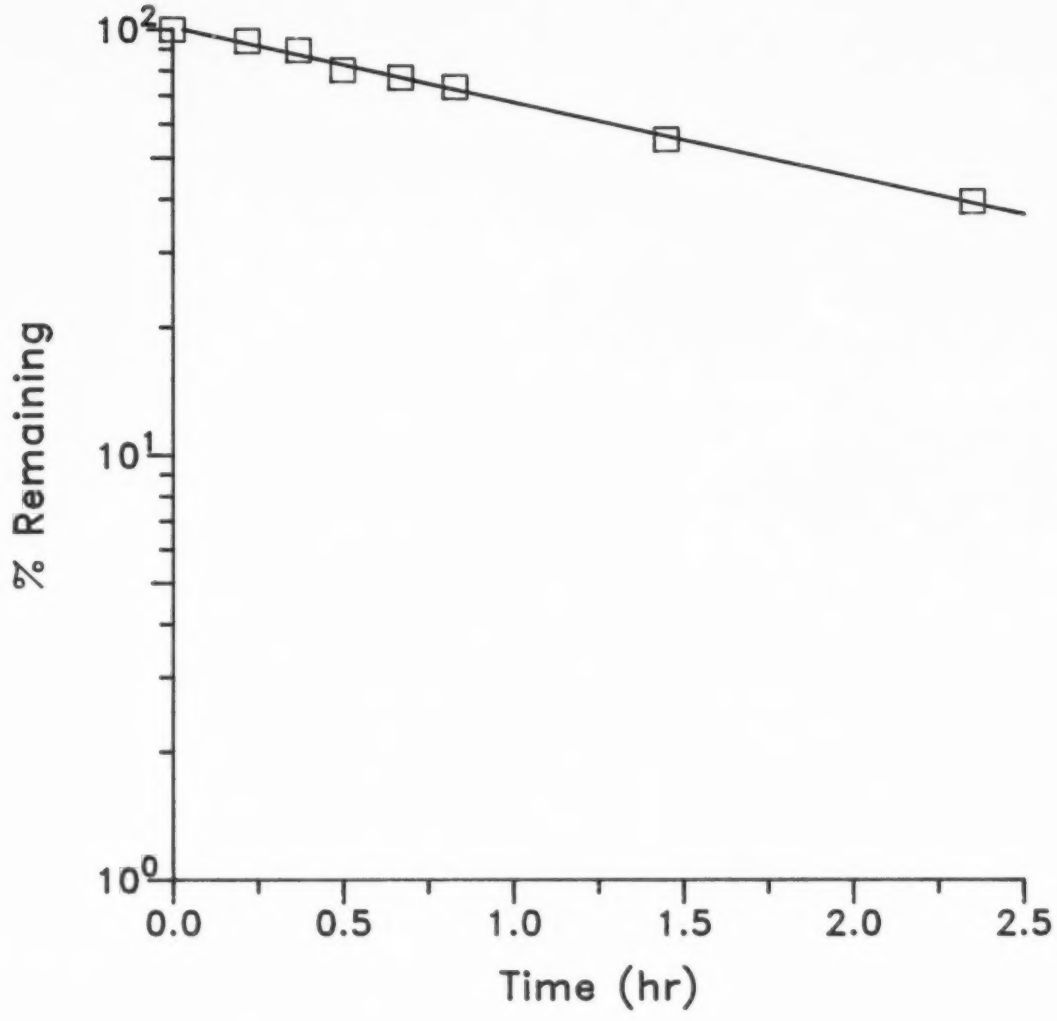


Figure 5.3.25 Hydrolysis of Uracil Mustard at 22.2°C, pH 7.03

5.3.26 Ethyl Carbamate
CAS No. 51-79-6

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^3K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3 (see below)					
7 (see below)					
9.50	87.0	10.4	9.7	2.8	0.867
9.77	68.0	2.4	2.9	11.8	0.936

pH 3: Assuming a loss of 2% during 13 day run at 87°C yields $K_1 = 1.55 \times 10^{-3}d^{-1}$ and $t_{1/2}$ = >447 days.

pH 7: Assuming a loss of 10% during 13 day run at 87°C yields $K_1 = 8.1 \times 10^{-3}d^{-1}$ and $t_{1/2}$ = >85 days.

Comments: Calculated E_a = 15.5±0.3 K_{cal}/mole, log A = 10.4±1.2 and K_2 = 0.11 $M^{-1}hr^{-1}$ at 25°C.

Water Solubility: 2000 g/l

Source: Chem. Serv.

Listed Purity: Unknown

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 8 ppm

Analytical Procedure: Direct aqueous injections of on microliter aliquots were made on-column. Acrylamide was added to each tube before analysis.

Extraction Solvent: NA

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: FID

Column: DB Wax+, 30M, 1 micron, 0.53 mm ID

Temperature Program: 95°C to 190°C

Mobile Phase: NA

Internal Standard: Acrylamide at 6.8 ppm

Linear Range of Analysis:

5.3.26 Ethyl Carbamate

$K_1 = 2.4 \times 10^{-3}\ hr^{-1}$
$T_{1/2} = 11.8$ days
$R^2 = 0.936$

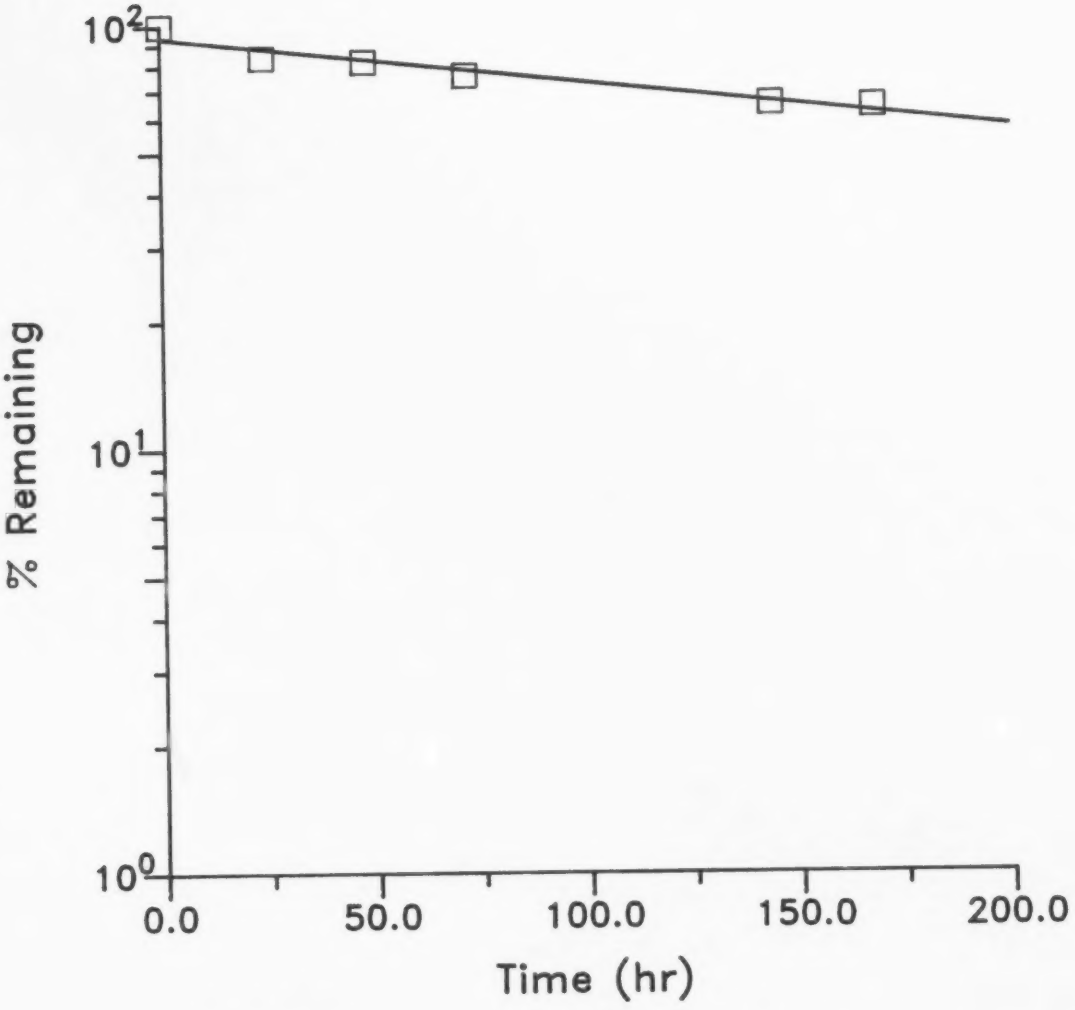


Figure 5.3.26 Hydrolysis of Ethyl Carbamate at 68°C, pH 9.77

5.3.27 1,3-Dichloro-2-propanol
CAS No. Reference 616-23-9

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^2K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(hr)$	r^2
7.02	68.0	43.5		1.58	0.994
7.02	68.0	46.8		1.48	0.997
7.02	68.0	41.9		1.65	0.927
10.04	25.0	37.1	976	1.87	0.914
10.04	25.0	32.5	855	2.14	0.973
10.04	25.0	30.6	805	2.26	0.972
10.04	25.0	29.6	780	2.33	0.984

Water Solubility: 1 in 10 parts water

Source: Aldrich

Listed Purity: 95%

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 19.3 ppm

Analytical Procedure: Direct aqueous cool on-column injections of the buffered solutions.

Extraction Solvent: NA

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: FID

Column: DB Wax+, 30M, 1 micron film, 0.53 mm ID

Temperature Program: 95°C to 140°C

Mobile Phase: NA

Internal Standard: 2,3-Dichloro-1-propanol at 19.6 ppm

Linear Range of Analysis:

5.3.28 2,3-Dichloro-1-propanol
CAS No. Reference 616-23-9

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^3K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
7.02	68.0	8.1		3.6	0.959
7.02	68.0	8.2		3.5	0.985
7.02	68.0	7.4		3.9	0.981
7.02	68.0	6.2		4.7	0.931
11.00	26.0	19.3	19.3	1.5	0.728
11.00	26.0	19.9	19.9	1.5	0.999
11.00	26.0	20.1	20.1	1.4	0.996
11.00	26.0	23.1	23.1	1.3	0.934

Water Solubility: 1 part in 10 parts water

Source: Kodak

Listed Purity: Unknown

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 19.6

Analytical Procedure: Same as 1,3-Dichloro-2-propanol

Extraction Solvent: NA

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: FID

Column: DB Wax+, 0.53 mm 1.0 u film thickness

Temperature Program: 95° - 140°C

Mobile Phase:

Internal Standard: 1,3-Dichloro-2-propanol 19.3 ppm

Linear Range of Analysis:

5.3.28 2,3-Dichloro-1-propanol

$K_1 = 1.12 \times 10^{-2}\ hr^{-1}$
$T_{1/2} = 2.6$ days
$R^2 = 0.999$

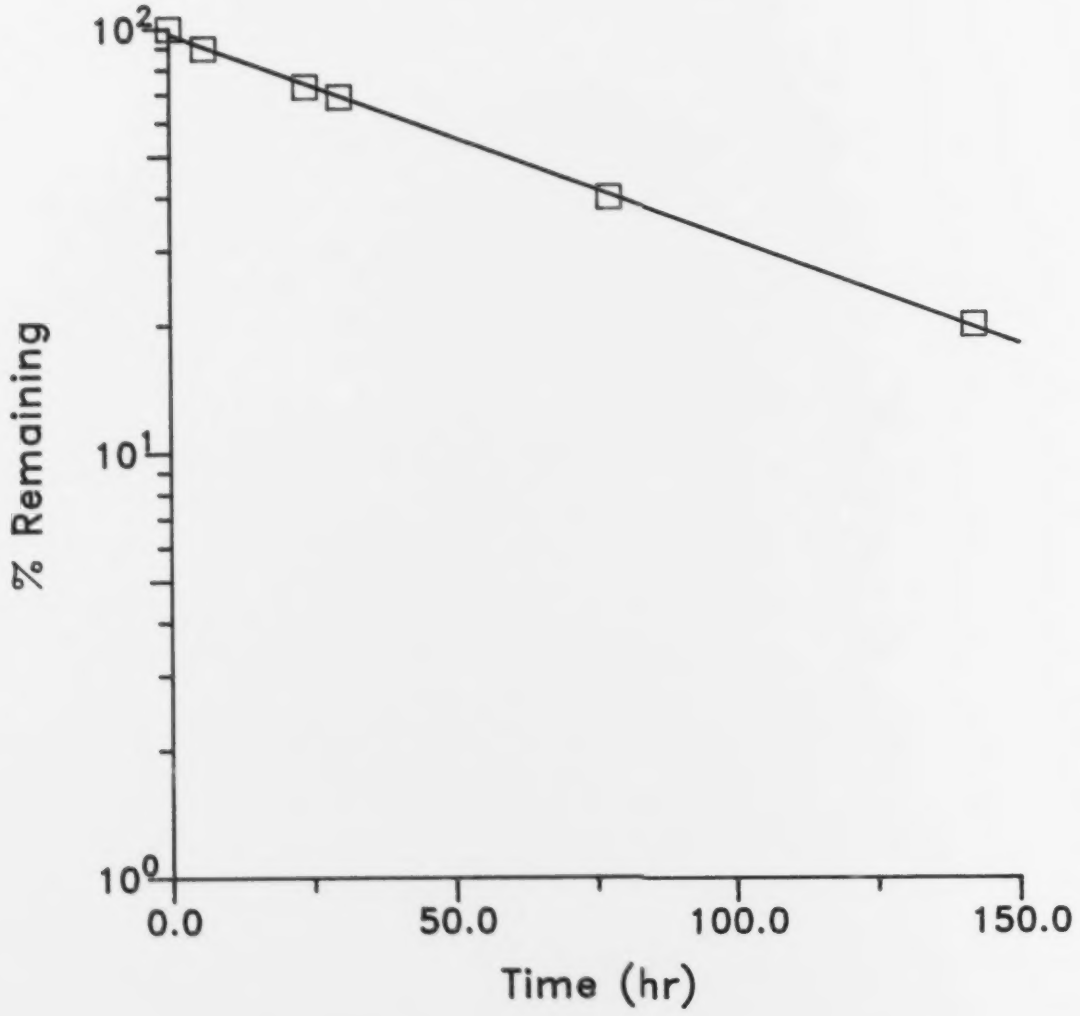


Figure 5.3.28 Hydrolysis of 2,3-Dichloro-1-propanol at 24°C, pH 11.0

5.3.29 1,2,3-Trichloropropane
CAS No. 96-18-4

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^2K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.04	87.0	0.50		5.8	0.841
3.07	87.0	0.14		21.1	0.876
7.12	87.0	0.24		11.6	0.930
7.11	87.0	0.42		6.7	0.793
10.53	68.0	9.6	18	0.30	0.998
9.63	87.0	97	671	0.03	0.991
9.71	87.0	105	604	0.03	0.999

Comment: An activation energy of 45.8±1.9 Kcal/mole was calculated for the alkaline hydrolysis of pronamide and log A = 30.72±0.29. The alkaline contribution to the observed neutral hydrolysis rate was calculated to be 25%.

Water Solubility:

Source: Chem. Serv.

Listed Purity: Unknown

Identity-Purity by Spectral Analysis: Appendix A

Analysis Concentration: 0.9 ppm

Analytical Procedure: Ten (10) ml of the buffered hydrolysis sample is extracted with 2 ml of iso-octane (0.7 ppm in cis-1,4-dichloro-2-butene). The extract is diluted 1:5 before analysis by GC.

Extraction Solvent: Iso-octane

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: EC

Column: OV-1, 5M, 2.65 micron film, 0.53 mm ID

Temperature Program: 45°C isothermal

Mobile Phase: NA

Internal Standard: cis-1,4-Dichloro-2-butene (0.7 ppm in iso-octane)

5.3.29 1,2,3–Trichloropropane

K_1 = 1.05 hr^{-1}
$T_{1/2}$ = 0.03 days
R^2 = 0.999

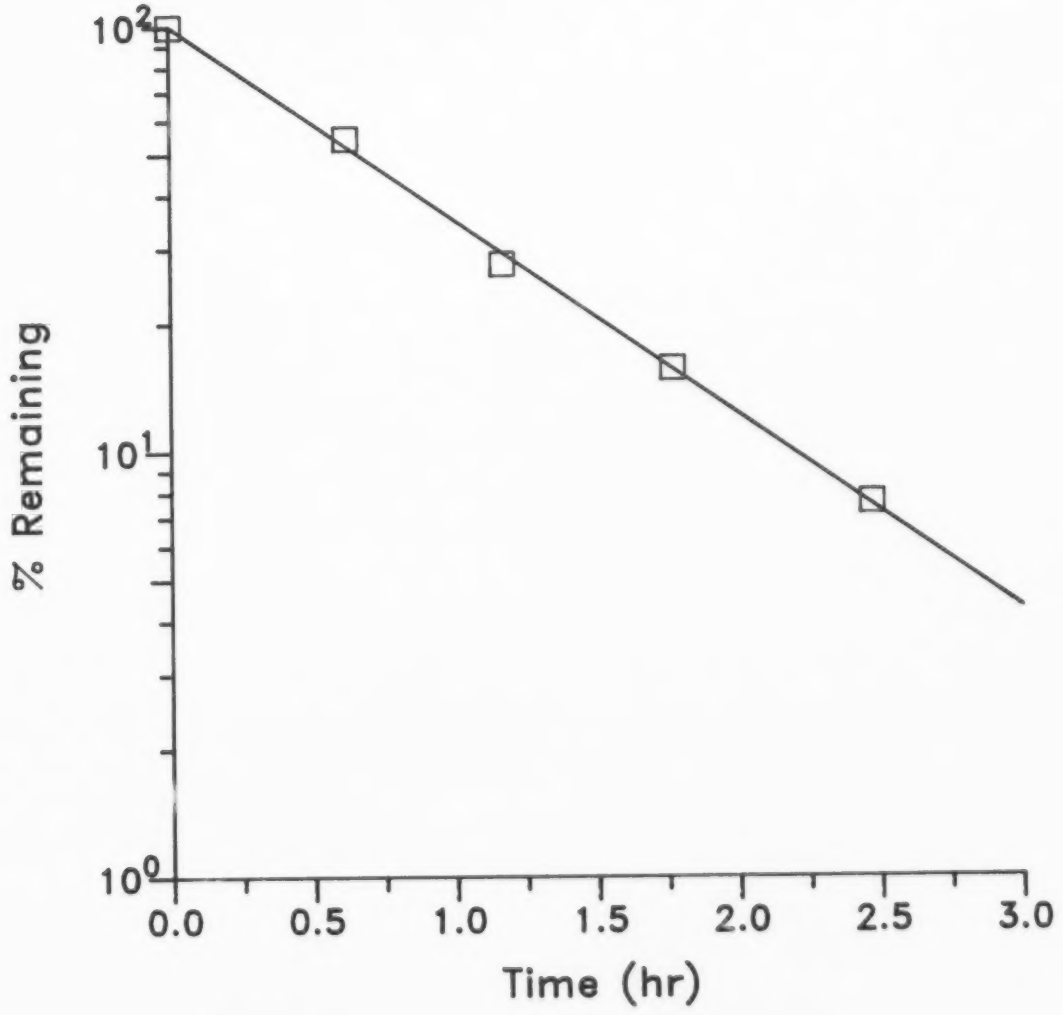


Figure 5.3.29 Hydrolysis of 1,2,3–Trichloropropane at 87°C, pH 9.71

5.3.30 1,2,3-Trichlorobenzene[1]
CAS No. Reference 12002-48-1

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^3K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.03	68.0	7.80		3.7	0.755
3.08	70.0	0.79		36.6	0.420
3.07	70.0	1.50		19.2	0.933
3.07	70.0	0.88		32.8	0.691
6.99	68.0	3.28		8.8	0.688
7.13	70.0	0.80		36.1	0.740
7.13	70.0	1.93		15.0	0.867
7.10	70.0	1.90		15.2	0.691
10.70	68.0	3.81		7.6	0.533
9.80	70.0	0.84		34.4	0.626
9.74	70.0	3.0		9.6	0.603

Water Solubility: 12 mg/l

Source: Aldrich

Listed Purity: 99%

Identity-Purity by Spectral Analysis: Appendices A and B

Analysis Concentration: 146 ppm

Analytical Procedure: At the time of analysis of each tube, the buffered solution of TCB was extracted with iso-octane made to 635 ppb with 2,4-dichlorotoluene (IS). Dilution 1:5 with iso-octane gave final concentrations of 127 ppb IS and 10 ppb of TCB.

Extraction Solvent: iso-octane

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: EC

Column: DB-5, 30M, .32 mm, .25 u film thickness

---

[1] CAS No. 12002-48-1 in OSW list references "trichlorobenzenes"

5.3.30 1,2,3-Trichlorobenzene (Continued)

Temperature Program: 100°C Iso

Mobile Phase: NA

Internal Standard: 2,4-Dichlorotoluene (635 ppb in iso-octane)

Linear Range of Analysis:

5.3.30 1,2,3–Trichlorobenzene

K_1 = 1.5 x 10^{-3} hr
$T_{1/2}$ = 19.2 days
R^2 = 0.933

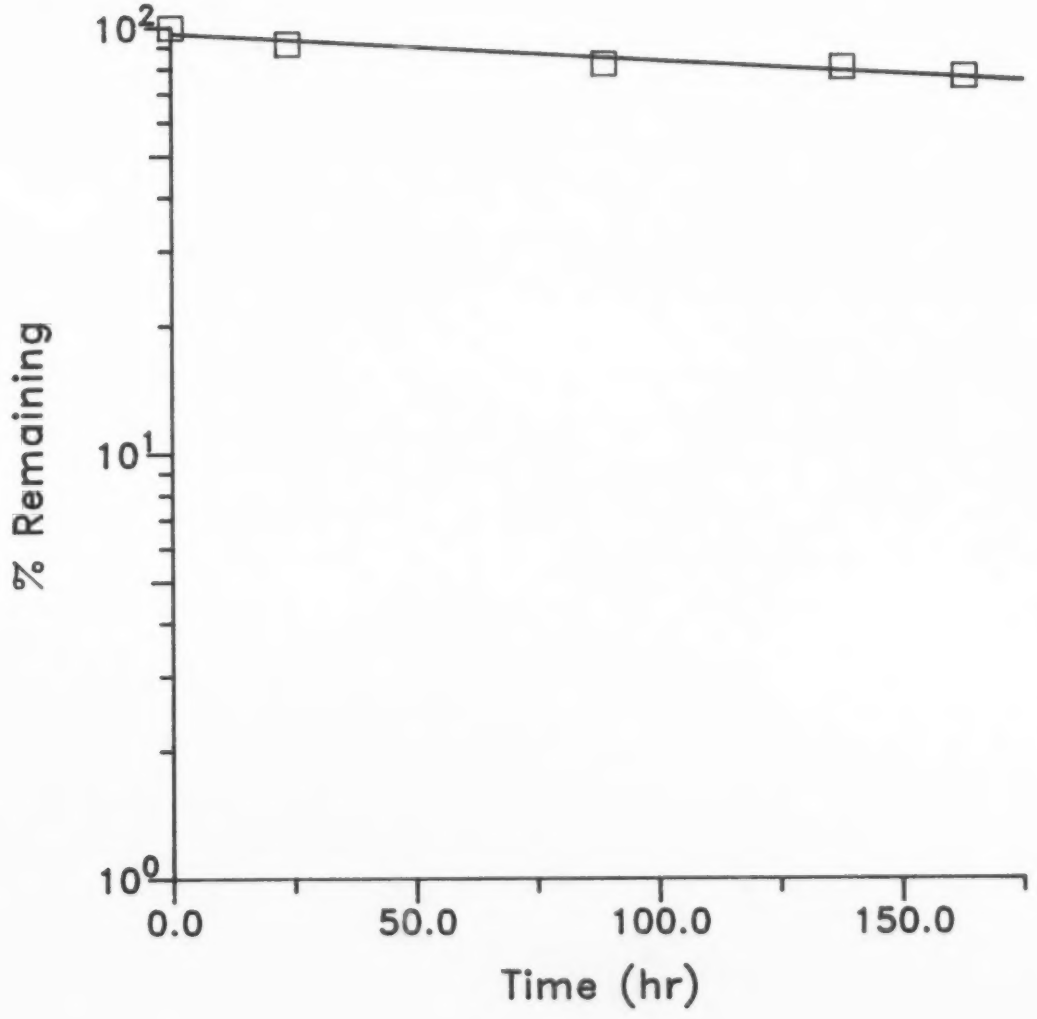


Figure 5.3.30 Hydrolysis of 1,2,3–Trichlorobenzene at 70°C, pH 3.07

5.3.31 1,2,4-Trichlorobenzene[1]
CAS No. Reference 12002-48-1

HYDROLYSIS AND ANALYSIS DATA

Hydrolysis Data:

pH	Temp, °C	$10^3K_1(hr^{-1})$	$K_2(M^{-1}hr^{-1})$	$t_{1/2}(d)$	r^2
3.03	68.0	4.4		6.5	0.593
3.09	70.0	2.6		11.1	0.636
3.09	70.0	2.9		10.0	0.628
3.10	70.0	1.6		18.4	0.773
6.99	68.0	3.6		8.1	0.551
7.11	70.0	4.4		6.6	0.888
7.11	70.0	6.7		4.3	0.530
7.09	70.0	2.0		14.5	0.471
10.70	68.0	4.2		6.9	0.693
9.77	70.0	4.9		5.9	0.999
9.81	70.0	3.7		7.7	0.811
9.81	70.0	2.5		11.5	0.813

Water Solubility: 19 mg/l

Source: Chem. Serv.

Listed Purity: Unknown

Identity-Purity by Spectral Analysis: Appendices A and B

Analysis Concentration: 155 ppm

Analytical Procedure: See 1,2,3-Trichlorobenzene

Extraction Solvent:

Instrumentation: GC X HPLC ___ IC ___ Diode Array UV ___

Detector: EC

Column: DB-5, 30M, .32 mm, .25 m film thickness

Temperature Program: 100°C Iso

---

[1] CAS No. 12002-48-1 in OSW list references "Trichlorobenzenes"

5.3.31 1,2,4-Trichlorobenzene (Continued)

Mobile Phase: NA

Internal Standard: 2,4-Dichlorotoluene (635 ppb in iso-octane)

Linear Range of Analysis:

5.3.31 1,2,4–Trichlorobenzene

$K_1 = 4.4 \times 10^{-3}\ hr^{-1}$
$T_{1/2} = 6.6$ days
$R^2 = 0.888$

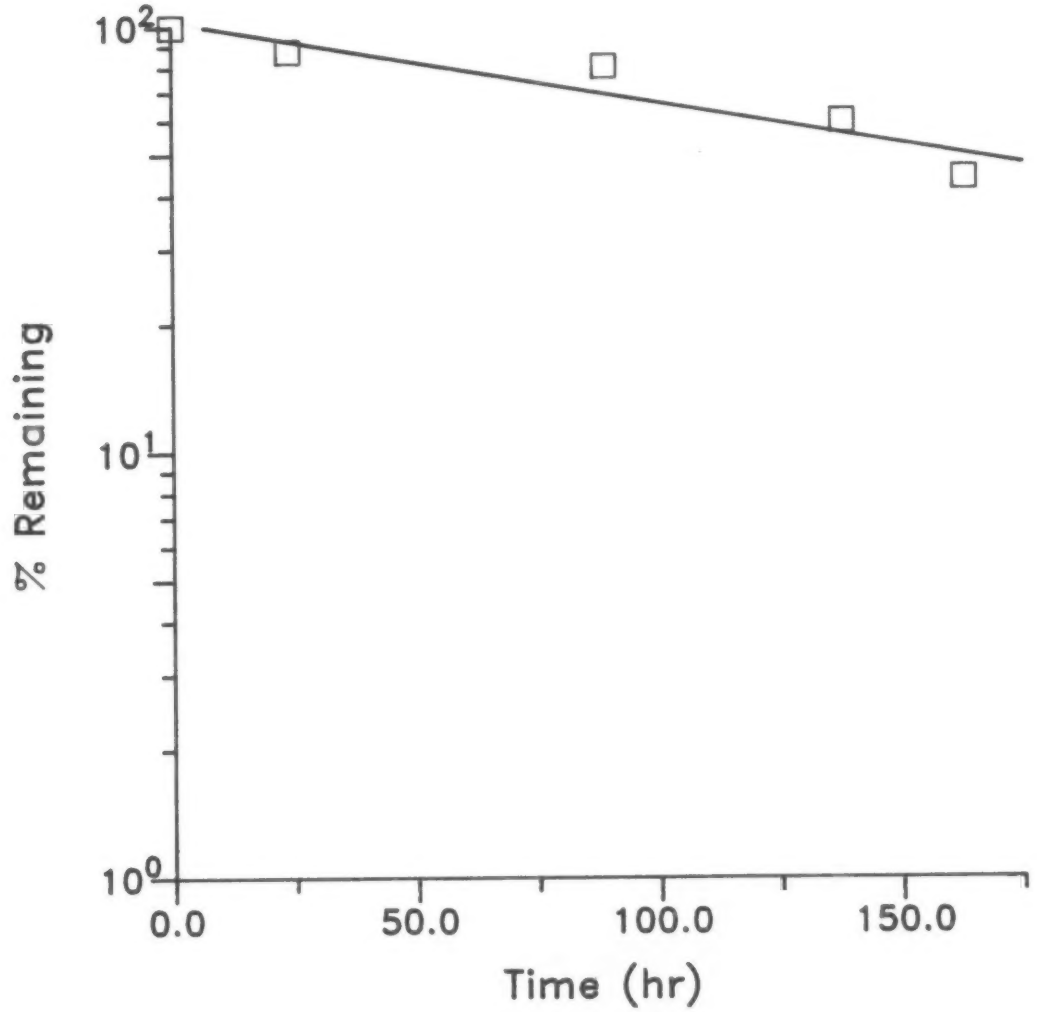


Figure 5.3.31 Hydrolysis of 1,2,4–Trichlorobenzene at 70°C, pH 7.11

APPENDIX A

MASS SPECTROMETRIC ANALYSIS

The objective of this MS work is to determine the purity and check the identity of selected chemicals from those shown in Table 1. These compounds are used as standards for determining the OSW First Third hydrolysis rate constants. The mass spectrum of each standard was determined by either GC/MS or probe/MS.

Reagents -- A 300 ppm standard solution in methylene chloride of each chemical except brucine was made for GC/MS analysis.

The brucine standard was available only as the sulfate. Since brucine will not chromatograph as the sulfate, a portion was dissolved in water, made basic with sodium hydroxide, and extracted with methylene chloride, giving a solution of the free brucine in methylene chloride.

Apparatus and Conditions -- Analyses were carried out with a Finnigan Model 4500 gas chromatograph mass spectrometer interfaced to the Finnigan Incos Data System. The mass spectral matching program used the "1984 EPA/NIH Incos Compatible Library Containing 42,197 Mass Spectra" obtained from W. L. Budde of EMSL-Ci (EPA/NIH Library). The 1983 version of the bound "EPA/NIH Mass Spectral Database" and the 1985 version of the "Eight Peak Index of Mass Spectra" were also used as references. GC column was a DB-5 fused capillary 30m x 0.25mm; most chemicals were run 3 min @ 45°C, 45-280°C @ 10°/min. Acrylonitrile, acrylamide, and 2-methylacetonitrile, because of their volatility, were held for 2 min at 30°C, then temperature programmed to 100°C at 10°/min. Reserpine and warfarin were analyzed from a direct probe at 75-200°C.

RESULTS

Standard Reference Compounds

Benzyl chloride - The GC mass spectrum was a good match to the standard spectrum of benzyl chloride in the EPA/NIH Library. There are several chlorotoluene isomers that mass spectrometry cannot distinguish from benzyl chloride. The chromatogram showed no other compounds.

2,4-D methyl ester - The GC mass spectrum was a good match to the standard spectrum of 2,4-D methyl ester in the EPA/NIH Library. The chromatogram showed an additional small impurity peak (lower boiling but well separated from the major compound); the impurity spectrum had no database match but was very similar to the 2,4-D methyl ester spectrum, apparently an isomer. Judging by the total ion current of each peak, it is estimated the chemical is 97% 2,4-D methyl ester with a 3% impurity.

trans-4-Chlorostilbene oxide - The GC mass spectrum was not in any available database. However, the fragmentation pattern shows characteristics expected for trans-4-chlorostilbene oxide. There is a prominent molecular ion at m/z 230, with a chlorine isomer pattern indicating only one chlorine. The base peak is m/z 89, representing a phenyl-C group; ions at m/z 212, 201, and

195 represent fragmentation corresponding to losses of HOH, COH, and a chlorine, respectively. This fragmentation pattern is what one would expect for trans-4-chlorostilbene oxide. The chromatogram showed no other compounds.

OSW Chemicals

1. Warfarin - The probe mass spectrum was a good match to the standard spectrum of warfarin in the EPA/NIH Library. An overall estimate of the purity of the chemical could not be determined (except to say the chemical is mostly warfarin) since the analysis was by probe/MS.

2. Aldrin - The GC mass spectrum was a good match to the standard spectrum of aldrin in the EPA/NIH Library. The chromatogram showed no other compounds.

3. Brucine - The GC mass spectrum was a good match to the standard spectrum of brucine in the EPA/NIH Library. The chromatogram showed no other compounds (GC-pure). It must be remembered that the sample preparation would remove any highly polar impurities present in the starting sulfate.

4. Dieldrin - The GC mass spectrum was a good match to the standard spectrum of dieldrin in the EPA/NIH Library. The chromatogram showed no other compounds.

5. Disulfoton - The GC mass spectrum was a good match to the standard spectrum of disulfoton in the EPA/NIH Library. The chromatogram showed no other compounds.

6. Endosulfan I - The GC mass spectrum was a good match to the standard spectrum of endosulfan in the EPA/NIH Library. However, mass spectrometry by itself is unable to distinguish between the two isomers, endosulfan I and endosulfan II. The GC retention times of the endosulfan I and II both match established pesticide retention times. Endosulfan I elutes first and is well separated from endosulfan II. The chromatogram showed no other compounds.

7. Endosulfan II - The GC was a good match to the standard spectrum of endosulfan in the EPA/NIH Library. However, mass spectrometry by itself is unable to distinguish between the two isomers, endosulfan I and endosulfan II. The GC retention times of endosulfan I and II both match established pesticide retention times. Endosulfan I elutes first and is well separated from endosulfan II. The chromatogram showed no other compounds.

8. 2-Methyllactonitrile - There is no standard spectrum of 2-methyllactonitrile in the EPA/NIH Library. However, a good match was found in the 1983 EPA/NIH Mass Spectral Database. The chromatogram showed no other compounds.

9. Famphur - The GC mass spectrum was an excellent match to the standard spectrum of famphur in the EPA/NIH Library. The chromatogram showed an additional small impurity peak (higher boiling but well separated from the major compound); the impurity spectrum had no database match but was very similar to the famphur spectrum, apparently an isomer. Judging by the total ion current of each peak, it is estimated the chemical is 96% famphur with a 4% impurity.

10. Acrylamide - The GC mass spectrum was an excellent match to the standard spectrum of acrylamide in the EPA/NIH Library. The chromatogram showed no other compounds, indicating the sample is pure with regard to impurities that will pass through a gas chromatograph.

11. Acrylonitrile - The GC mass spectrum was a good match to the standard spectrum of acrylonitrile in the EPA/NIH Library. The chromatogram showed no other compounds.

12. cis-1,4-Dichloro-2-butene - The GC mass spectrum was a good match to the standard spectrum of dichlorobutene in the EPA/NIH Library. However, mass spectrometry is unable to distinguish among the more than twenty possible isomers. The chromatogram showed no other compounds when the standard was first run, but a repeat run made after the solution had stood for more than a month showed some trans isomer.

13. trans-1,4-Dichloro-2-butene - The GC mass spectrum was a good match to the standard spectrum of dichlorobutene in the EPA/NIH Library. However, like its cis isomer, mass spectrometry is unable to distinguish among the more than twenty possible isomers. The chromatogram showed no other compounds when first run, but a repeat run made after the solution had stood for more than a month showed some cis isomer.

14. 4,4'-Methylene-bis-(2-chloroaniline) - The GC mass spectrum was a good match to the standard spectrum of 4,4'-methylene-bis-(2-chloroaniline) in the EPA/NIH Library. The chromatogram showed no other compounds. There are several other potential isomers of methylene-bis-(chloroaniline). Mass spectrometry by itself can not distinguish among these isomers.

15. Pentachloronitrobenzene - The GC mass spectrum was a good match to the standard spectrum of pentachloronitrobenzene in the EPA/NIH Library. The chromatogram showed no other compounds.

16. Pronamide - The GC mass spectrum was a good match to the standard spectrum of pronamide in the EPA/NIH Library. The chromatogram showed no other compounds.

17. Reserpine - The probe mass spectrum was a poor match to the standard spectrum of reserpine in the EPA/NIH Library; the reference spectrum is poor because it lacks the logical base peak of m/z 195. A good match was found in the 1983 EPA/NIH Mass Spectral Database. An overall estimate of purity of the chemical could not be determined (except to say the chemical is mostly reserpine) since the analysis was by probe/MS.

18. Thiourea - The GC mass spectrum was a good match to the standard spectrum of thiourea in the EPA/NIH Library. The chromatogram showed no other compounds.

19. Ethyl carbamate - The GC mass spectrum was an excellent match to the standard spectrum of ethyl carbamate in the EPA/NIH Library. The chromatogram showed no other compounds.

20. 1,3-Dichloro-2-propanol - The GC mass spectrum was an excellent match to the standard spectrum of 1,3-dichloro-2-propanol in the EPA/NIH Library.

The chromatogram showed an additional small impurity peak higher boiling but well separated from the major compound; the spectrum of this small peak was an excellent match to the standard spectrum of 2,3-dichloro-1-propanol in the library. Judging by the total ion current of each peak, it is estimated that the chemical is 97% 1,3-dichloro-2-propanol and 3% 2,3-dichloro-1-propanol.

21. 2,3-Dichloro-1-propanol - The GC mass spectrum was a good match to the standard spectrum of 2,3-dichloro-1-propanol in the EPA/NIH Library. The chromatogram showed no other compounds.

22. 1,2,3-Trichloropropane - The GC mass spectrum was a good match to the standard spectrum of 1,2,3-trichloropropane in the EPA/NIH Library. The mass spectra of the trichloropropanes are distinctive, and there is no mistaking identification. The chromatogram showed no other compounds.

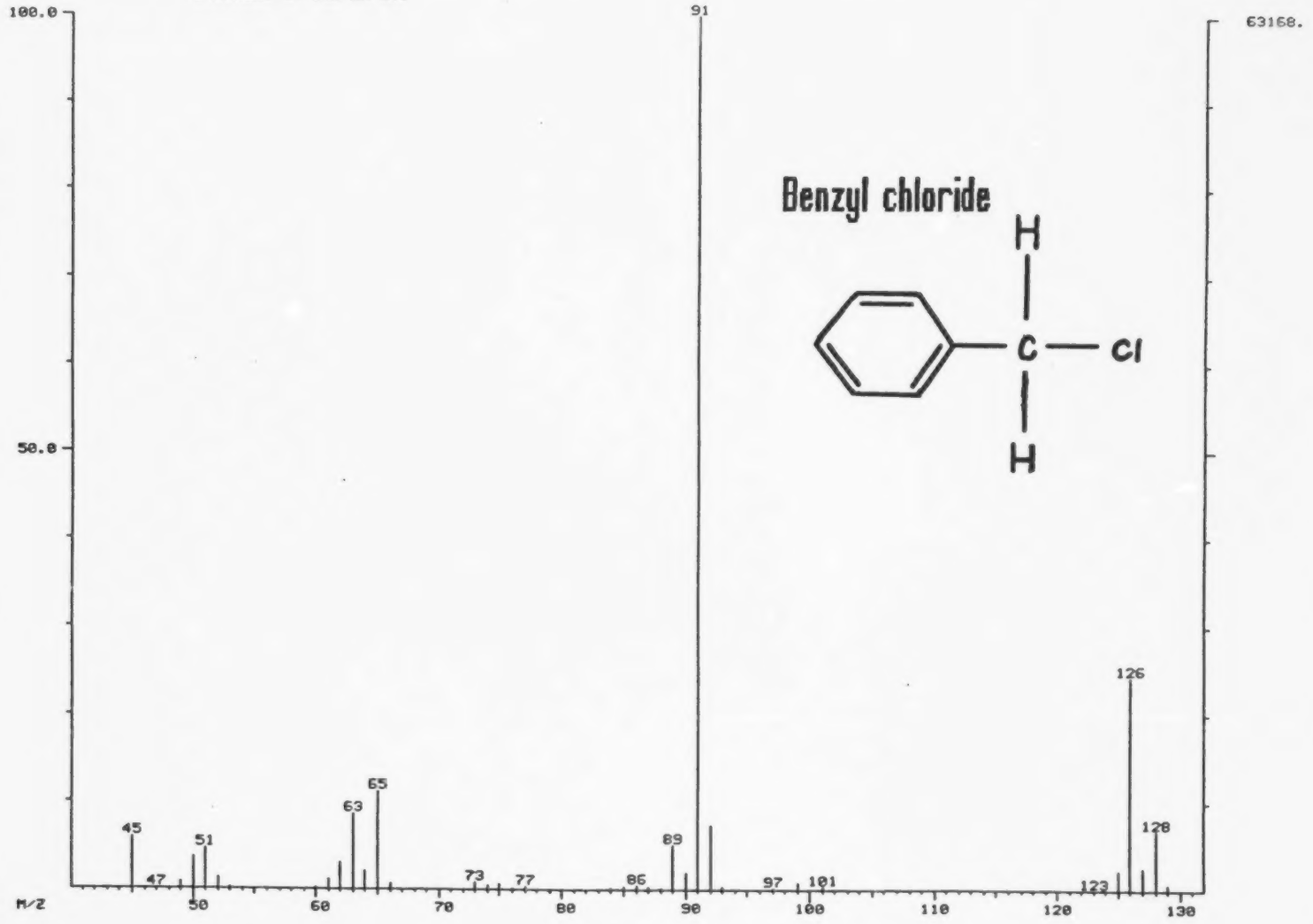
23. 1,2,3-Trichlorobenzene - The GC mass spectrum was a good match to the standard spectrum of trichlorobenzene in the EPA/NIH Library. However, mass spectrometry by itself is unable to distinguish among the three possible isomers. The chromatogram showed no other compounds.

24. 1,2,4-Trichlorobenzene - The GC mass spectrum was a good match to the standard spectrum of trichlorobenzene in the EPA/NIH Library. However, mass spectrometry by itself is unable to distinguish among the three possible isomers. The chromatogram showed no other compounds.

MASS SPECTRUM
03/20/86 13:50:00 + 6:10
SAMPLE: BENZYL CHLORIDE STD (300PPM) 3/17/86
CONDS.: EI
GC TEMP: 102 DEG. C
ENHANCED (S 15B 2N 0T)

DATA: BENZYL #370
CALI: CAL320 #3

BASE M/Z: 91
RIC: 126080.

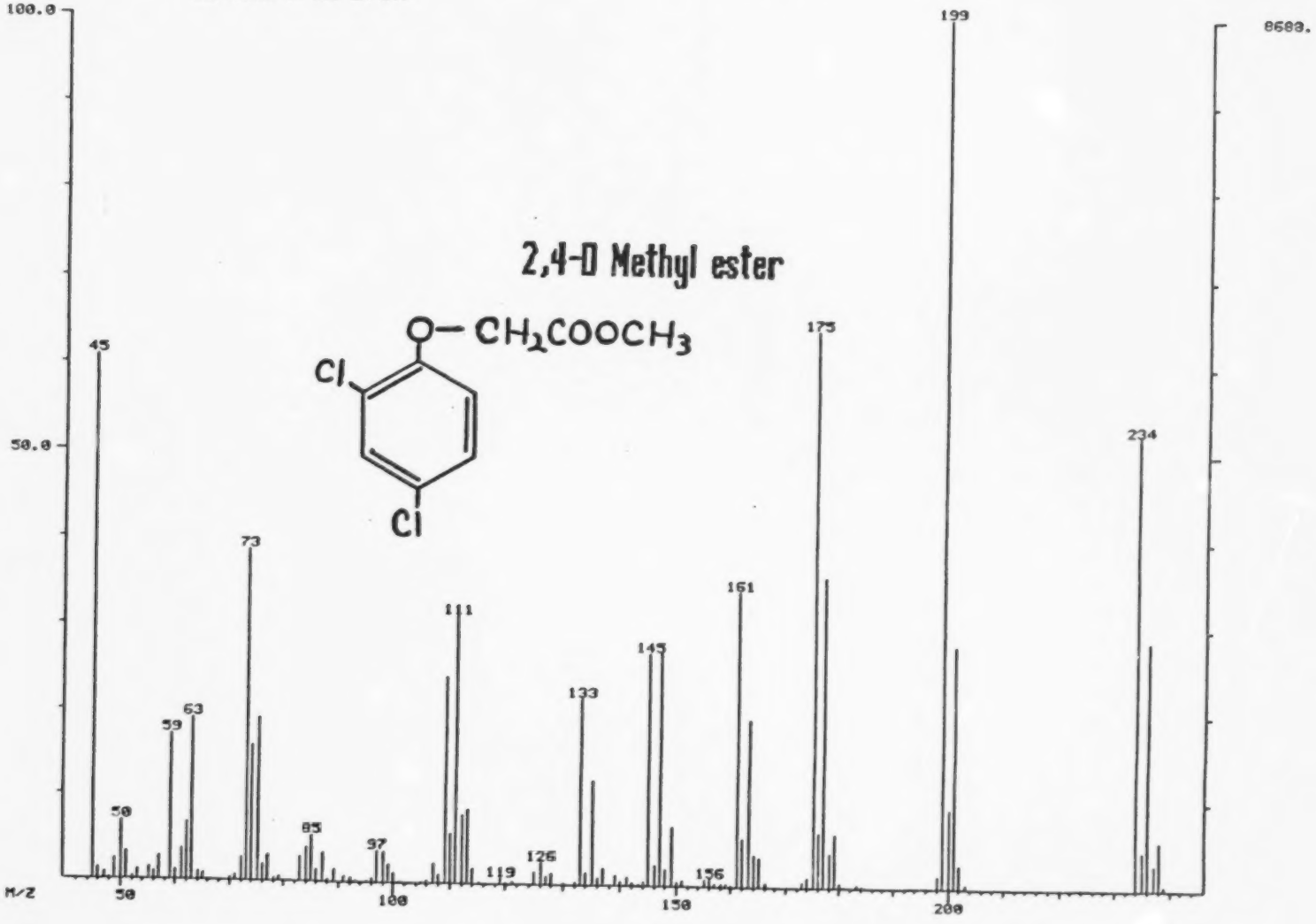


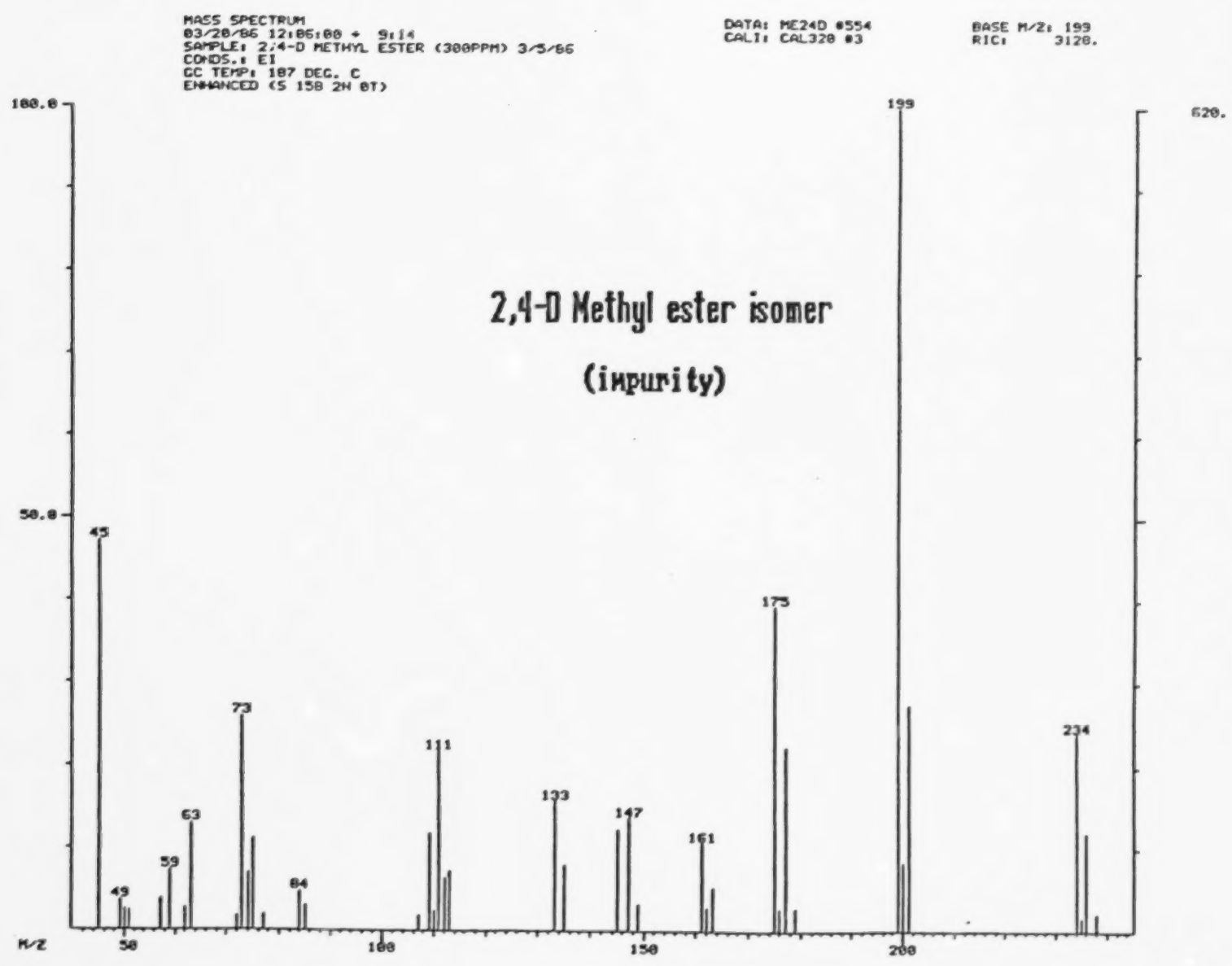
Benzyl chloride

MASS SPECTRUM
03/20/86 12:06:00 + 9:39
SAMPLE: 2,4-D METHYL ESTER (300PPM) 3/5/86
CONDS.: EI
GC TEMP: 192 DEG. C
ENHANCED (S 15B 2N 0T)

DATA: ME24D #573
CALI: CAL320 #3

BASE M/Z: 199
RIC: 75136.

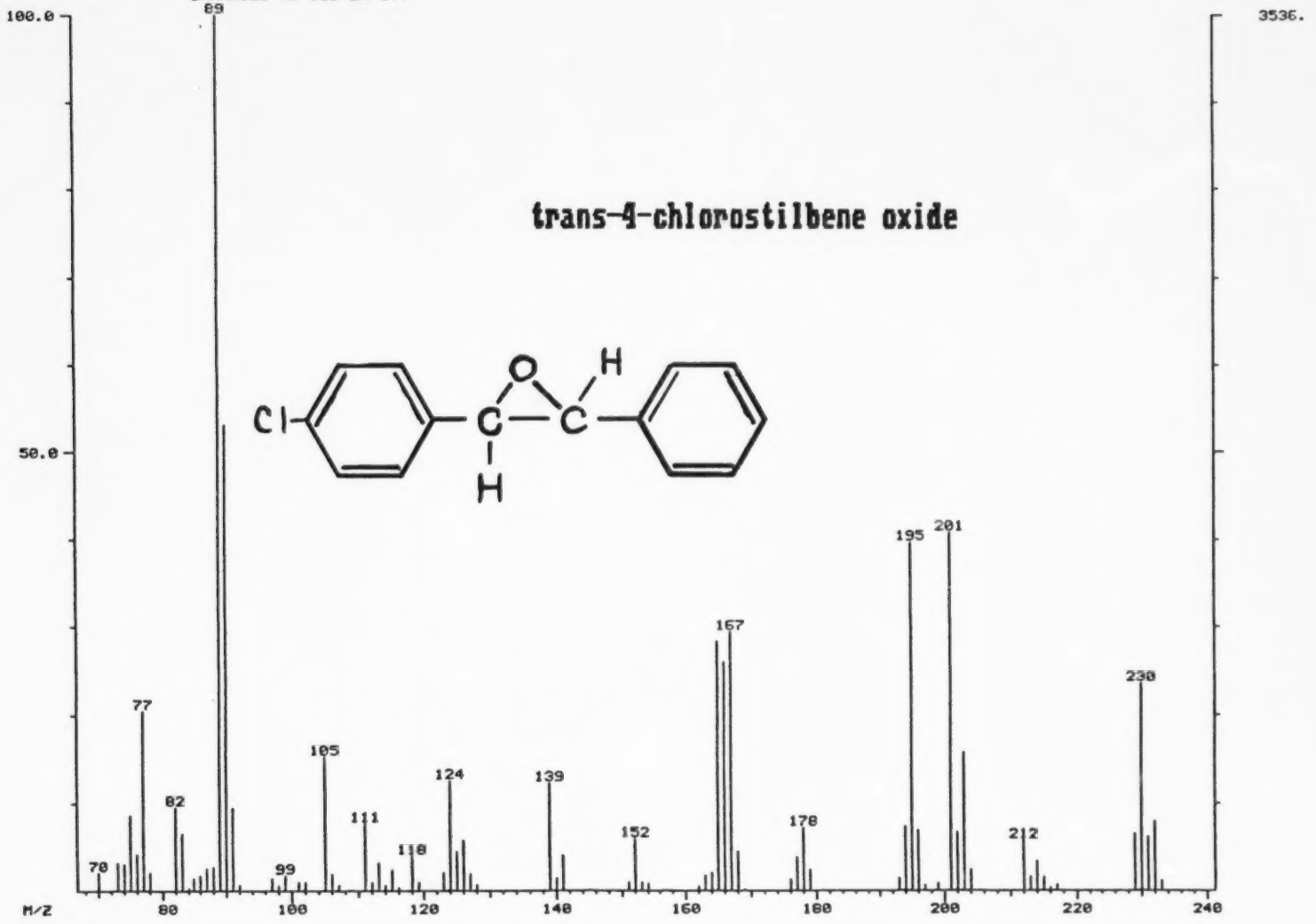



MASS SPECTRUM
03/20/86 12:06:00 + 9:14
SAMPLE: 2,4-D METHYL ESTER (300PPM) 3/5/86
CONDS.: E1
GC TEMP: 187 DEG. C
ENHANCED (S 15B 2H 8T)
DATA: ME24D #554
CALI: CAL320 #3
BASE M/Z: 199
RIC: 3120.
100.0
50.0
620.
2,4-D Methyl ester isomer
(impurity)
45
49
59
63
73
84
111
133
147
161
175
199
234
M/Z
50
100
150
200

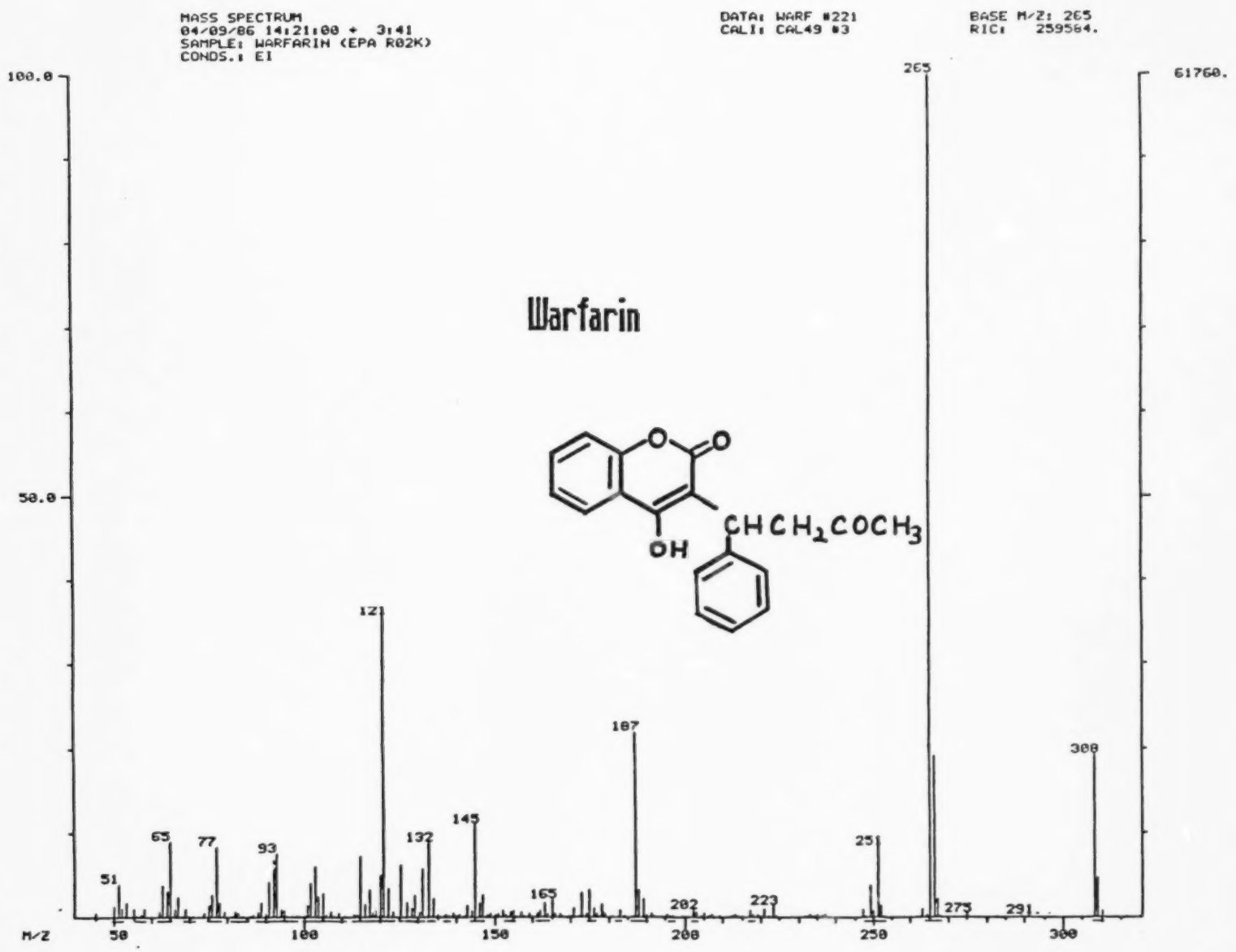
MASS SPECTRUM
03/20/86 11:39:00 + 12:26
SAMPLE: 4-CHLOROSTILBENEOXIDE (300PPM) 3/.10/86
CONDS.: EI
GC TEMP: 226 DEG. C
ENHANCED (S 15B 2N 0T)

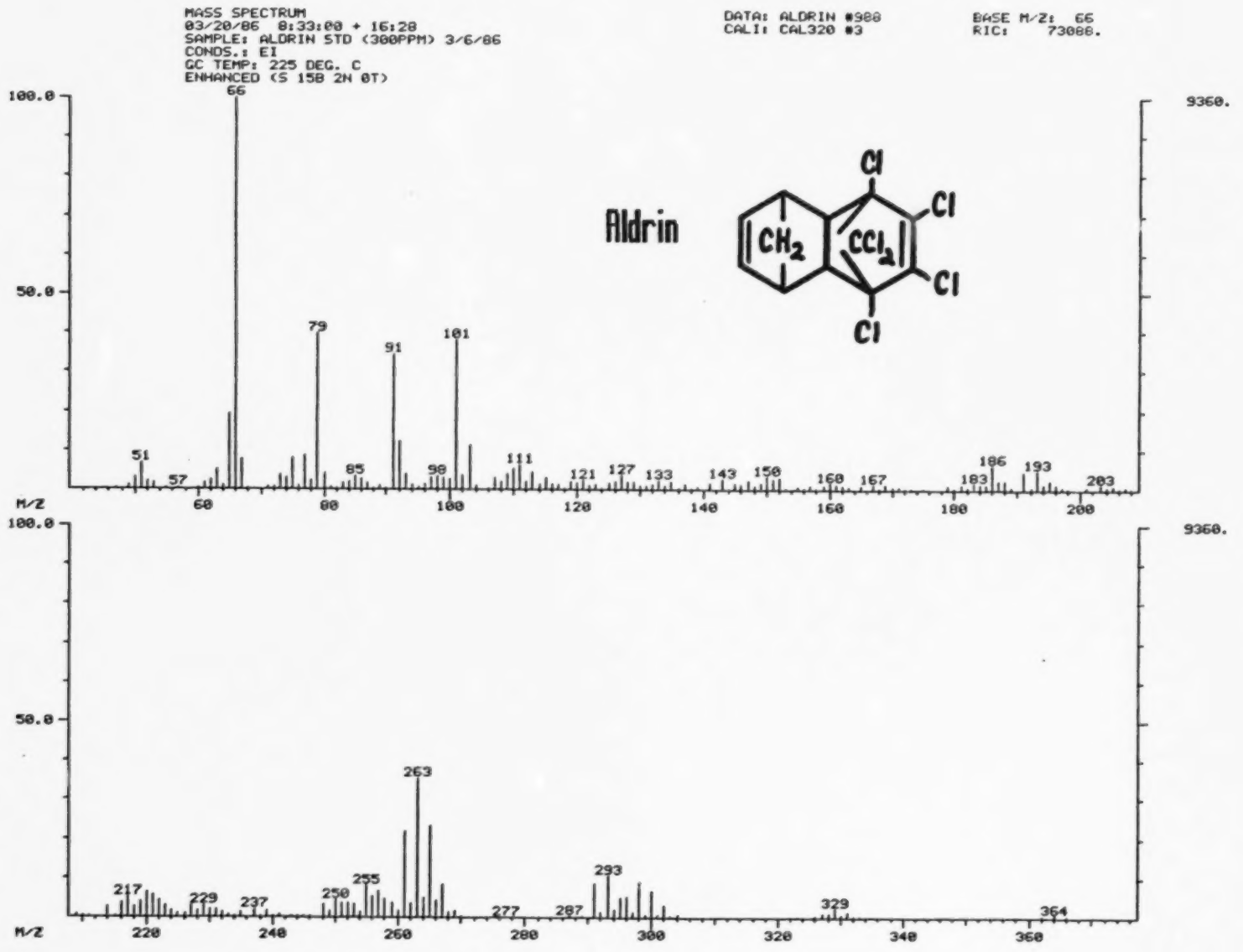
DATA: CHLOROSO #746
CALI: CAL320 #3

BASE M/Z: 89
RIC: 24768.



trans-4-chlorostilbene oxide


MASS SPECTRUM
04/09/86 14:21:00 + 3:41
SAMPLE: WARFARIN (EPA R02K)
CONDS.: EI
DATA: WARF #221
CALI: CAL49 #3
BASE M/Z: 265
RIC: 259564.
100.0
50.0
61760.
Warfarin
CHCH2COCH3
OH
O
O
265
121
187
308
145
132
65
77
93
51
165
202
223
251
273
291
M/Z
50
100
150
200
250
300

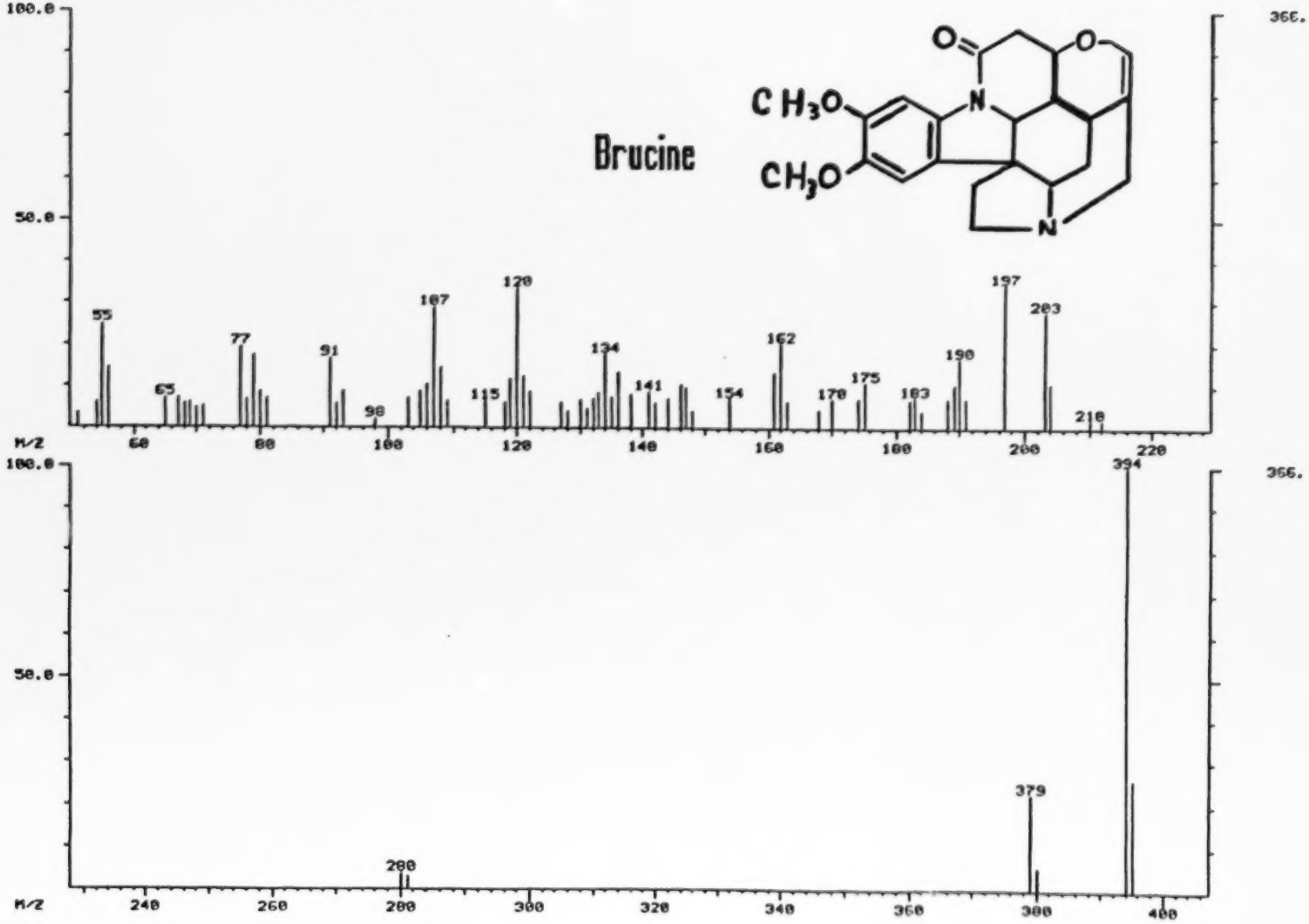

MASS SPECTRUM
03/20/86 8:33:00 + 16:28
SAMPLE: ALDRIN STD (300PPM) 3/6/86
CONDS.: EI
GC TEMP: 225 DEG. C
ENHANCED (S 150 2N 0T)
DATA: ALDRIN #900
CALI: CAL320 #3
BASE M/Z: 66
RIC: 73000.
Aldrin
Cl
Cl
Cl
Cl
CH2
CCl2
100.0
50.0
9360.
M/Z
66
79
91
101
51
57
85
98
111
121
127
133
143
150
160
167
183
186
193
203
60
80
100
120
140
160
180
200
263
217
229
237
250
255
277
287
293
329
364
220
240
260
280
300
320
340
360

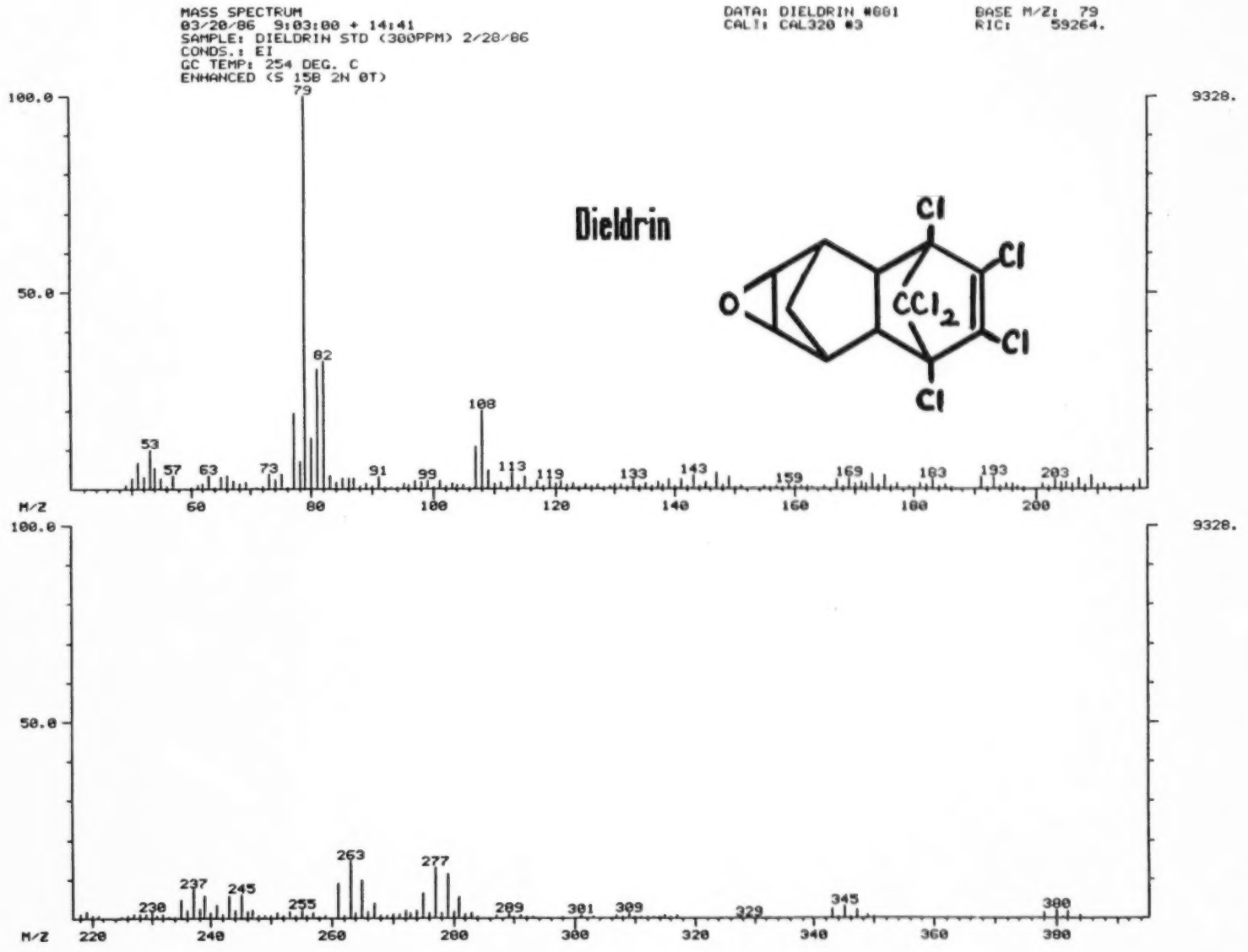
MASS SPECTRUM
04/09/86 9:25:00 + 20:43
SAMPLE: BRUCINE -NAOH, EXT TO MECL2
CONDS.: EI
GC TEMP: 201 DEG. C
ENHANCED (S 150 2N 0T)

DATA: BRUCIH3 #1243
CALI: CAL49 #3

BASE M/Z: 394
RIC: 3060.

Brucine

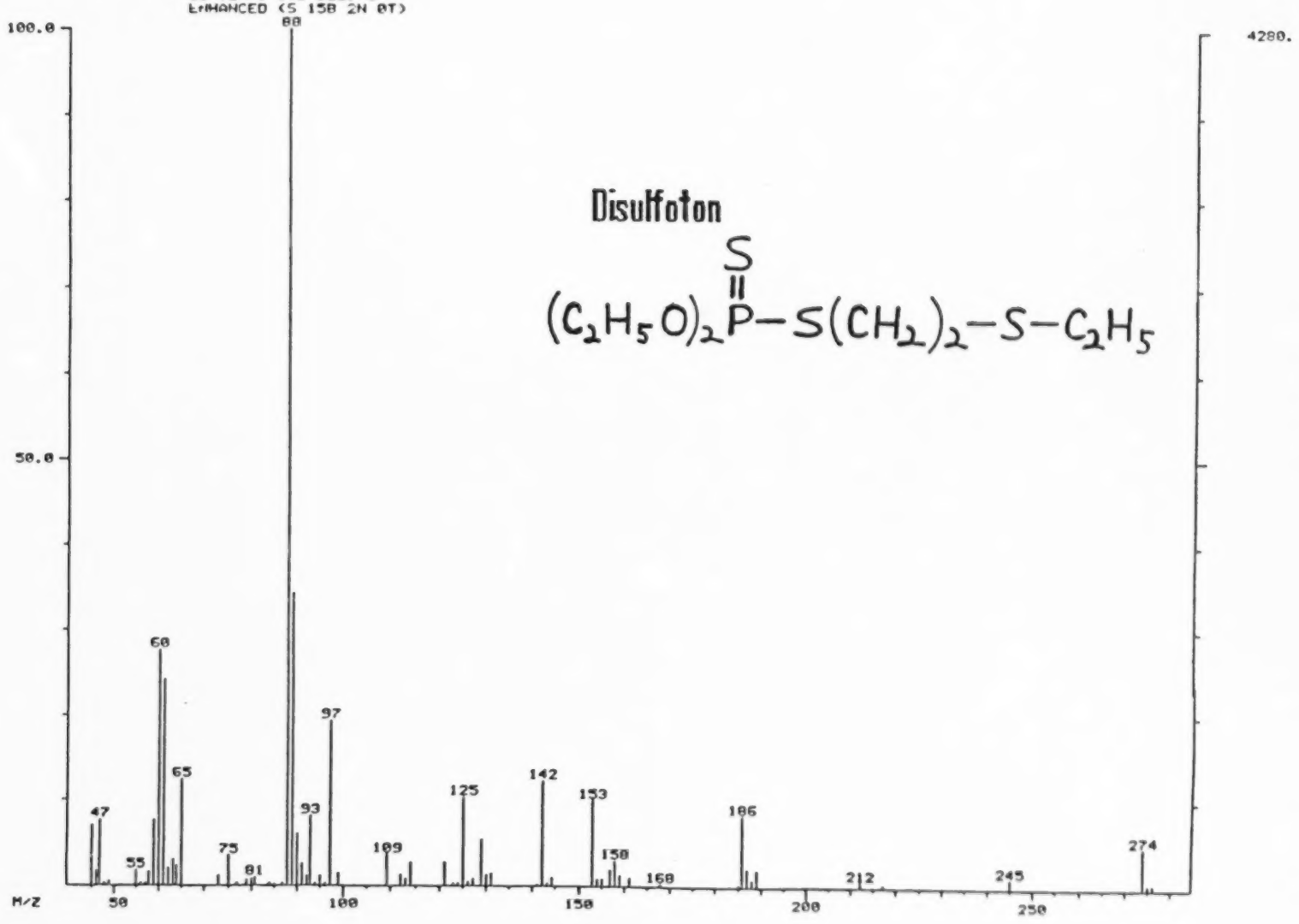



MASS SPECTRUM
03/20/86 9:03:00 + 14:41
SAMPLE: DIELDRIN STD (300PPM) 2/28/86
CONDS.: EI
GC TEMP: 254 DEG. C
ENHANCED (S 15B 2N 0T)
DATA: DIELDRIN #081
CALI: CAL320 #3
BASE M/Z: 79
RIC: 59264.
Dieldrin
Cl
Cl
Cl
Cl
O
CCl2
100.0
50.0
9320.
M/Z
79
82
108
53
57
63
73
91
99
113
119
133
143
159
169
183
193
203
60
80
100
120
140
160
180
200
263
277
237
245
230
255
289
301
309
329
345
380
220
240
260
280
300
320
340
360
380

MASS SPECTRUM
03/20/86 15:50:00 + 17:54
SAMPLE: DISOLFOTON (300PPM) 3/19/86
CONDS.: EI
GC TEMP: 162 DEG. C
ENHANCED (S 15B 2N 0T)

DATA: DISOL #1074
CALI: CAL320 #3

BASE M/Z: 88
RIC: 15760.



Disulfoton

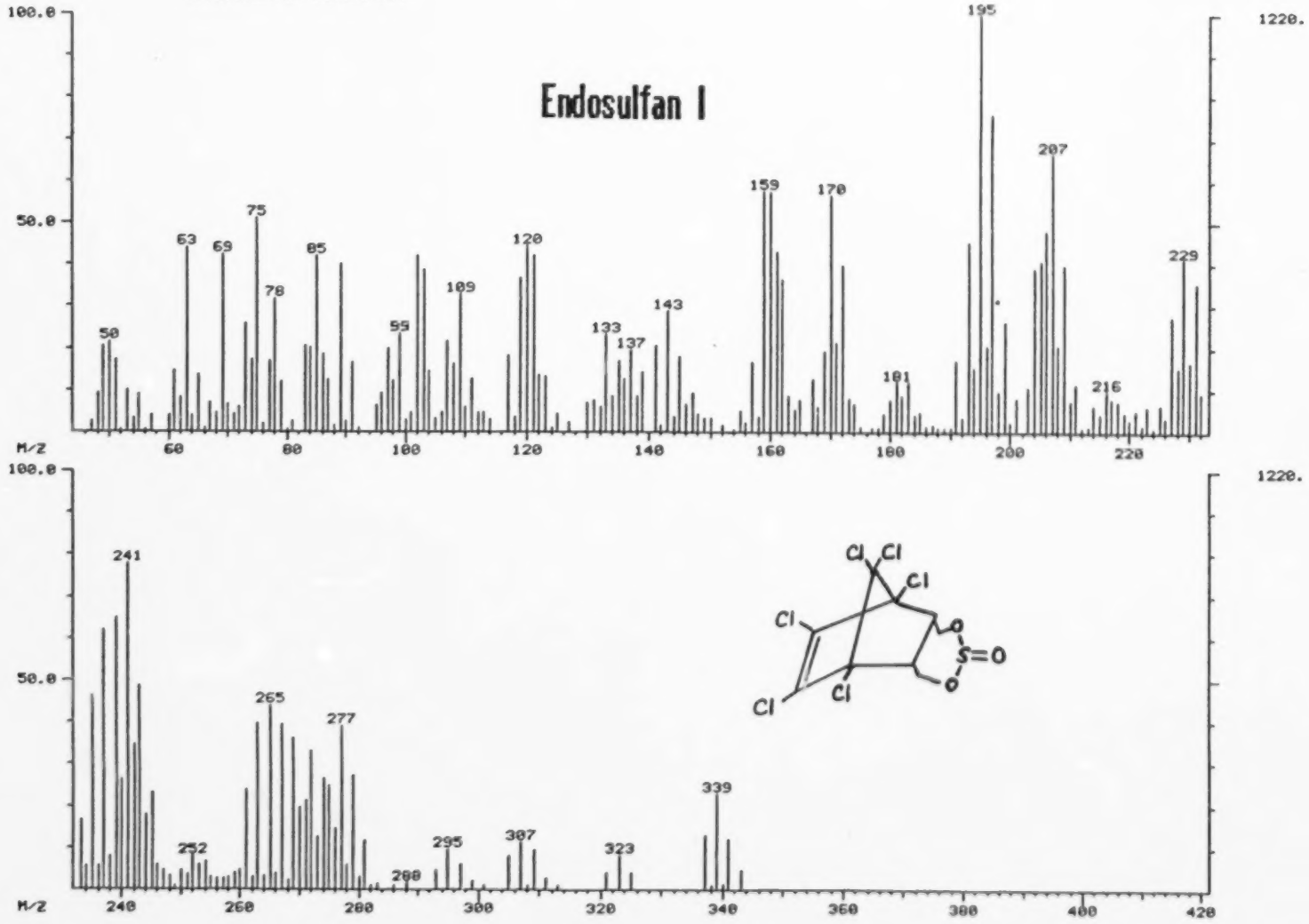
$$(C_2H_5O)_2\overset{\overset{S}{\|}}{P}-S(CH_2)_2-S-C_2H_5$$

MASS SPECTRUM
03/20/86 9:29:00 + 10:00
SAMPLE: ENDO1 STD (300PPM) 2/28/86
CONDS.: EI
GC TEMP: 249 DEG. C
ENHANCED (S 150 2N 0T)

DATA: ENDO1 #600
CALI: CAL320 #3

BASE M/Z: 195
RIC: 44460.

Endosulfan I

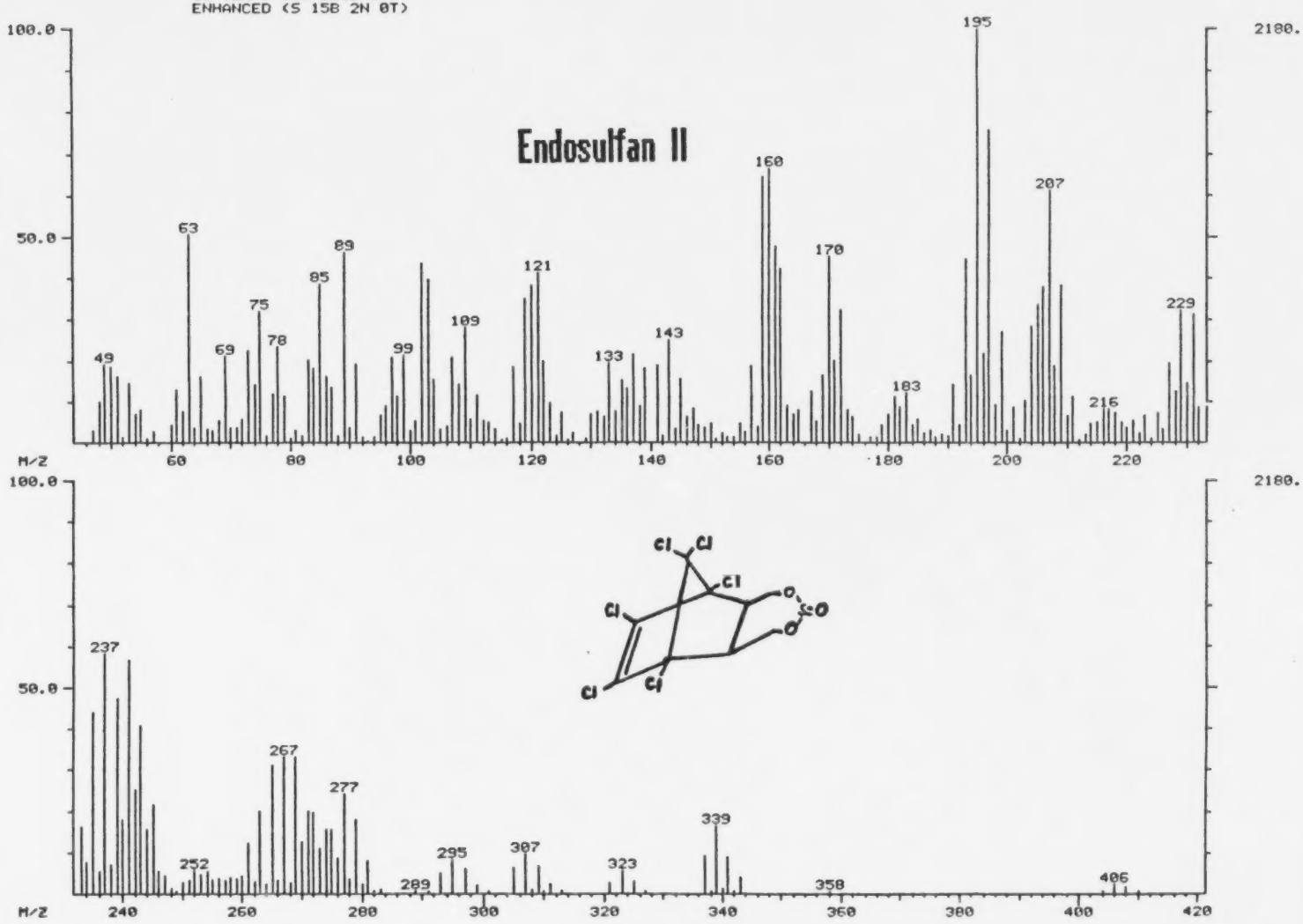


MASS SPECTRUM
03/20/86 9:50:00 + 11:05
SAMPLE: ENDO11 STD (300PPM) 2/28/86
CONDS.: EI
GC TEMP: 260 DEG. C
ENHANCED (S 15B 2N 0T)

DATA: ENDO11 #665
CALI: CAL320 #3

BASE M/Z: 195
RIC: 71808.

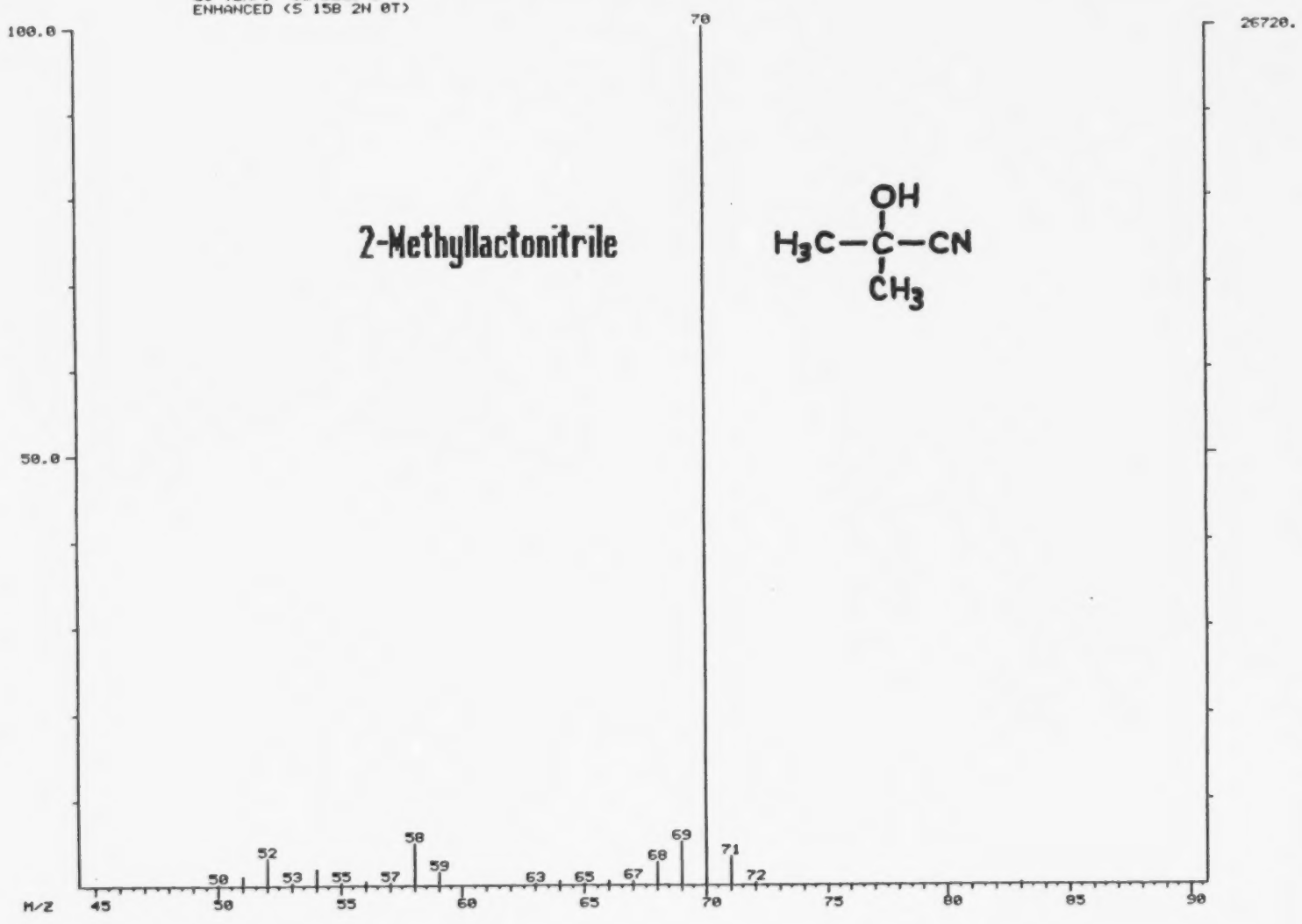
Endosulfan II



MASS SPECTRUM
03/20/86 15:19:00 + 2:51
SAMPLE: ACETONE CYANOHYDRIN (300PPM) 3/12/86
CONDS.: EI
GC TEMP: 62 DEG. C
ENHANCED (S 15B 2N 0T)

DATA: ACECY #171
CALI: CAL320 #3

BASE M/Z: 70
RIC: 34048.

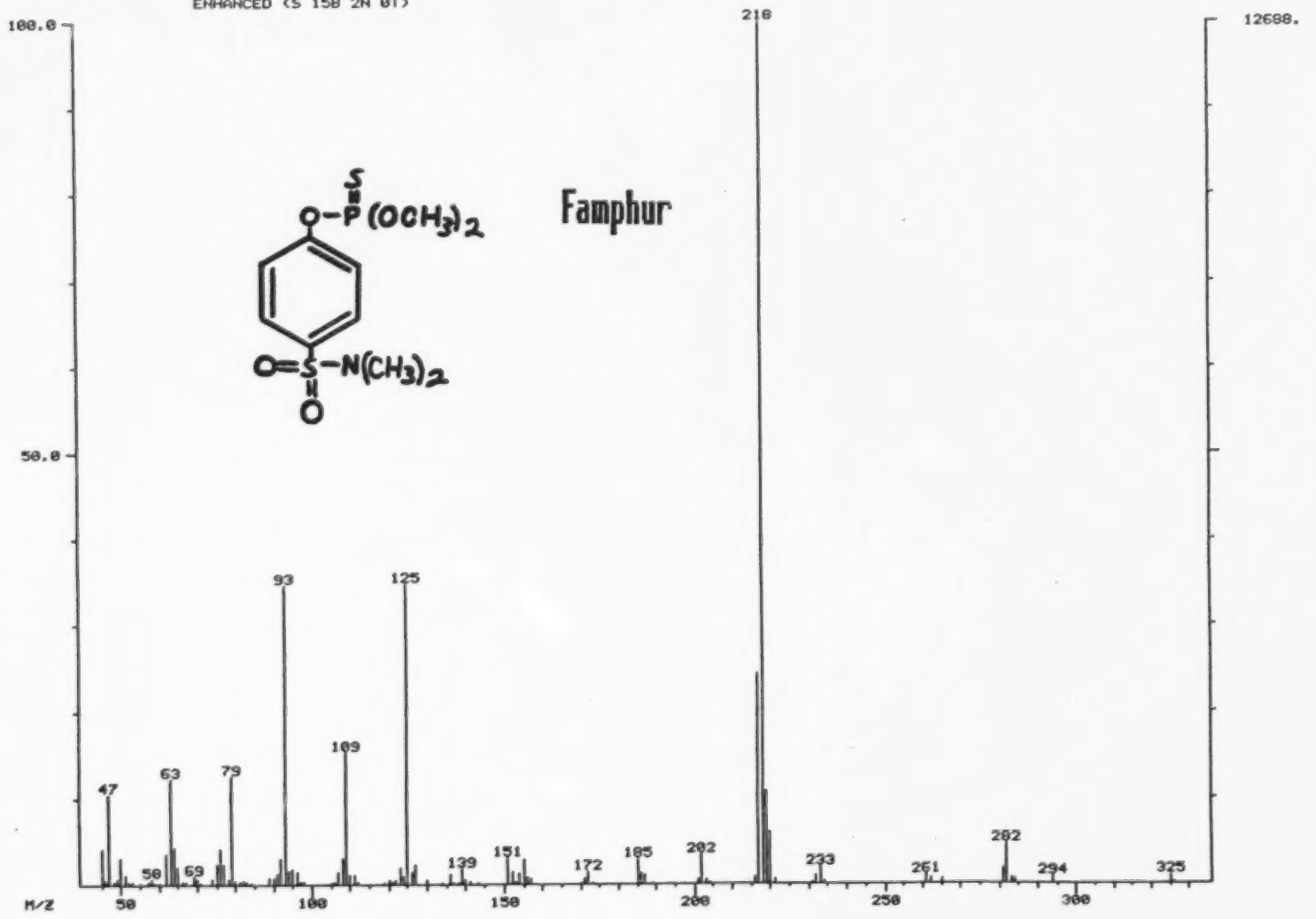


2-Methyllactonitrile

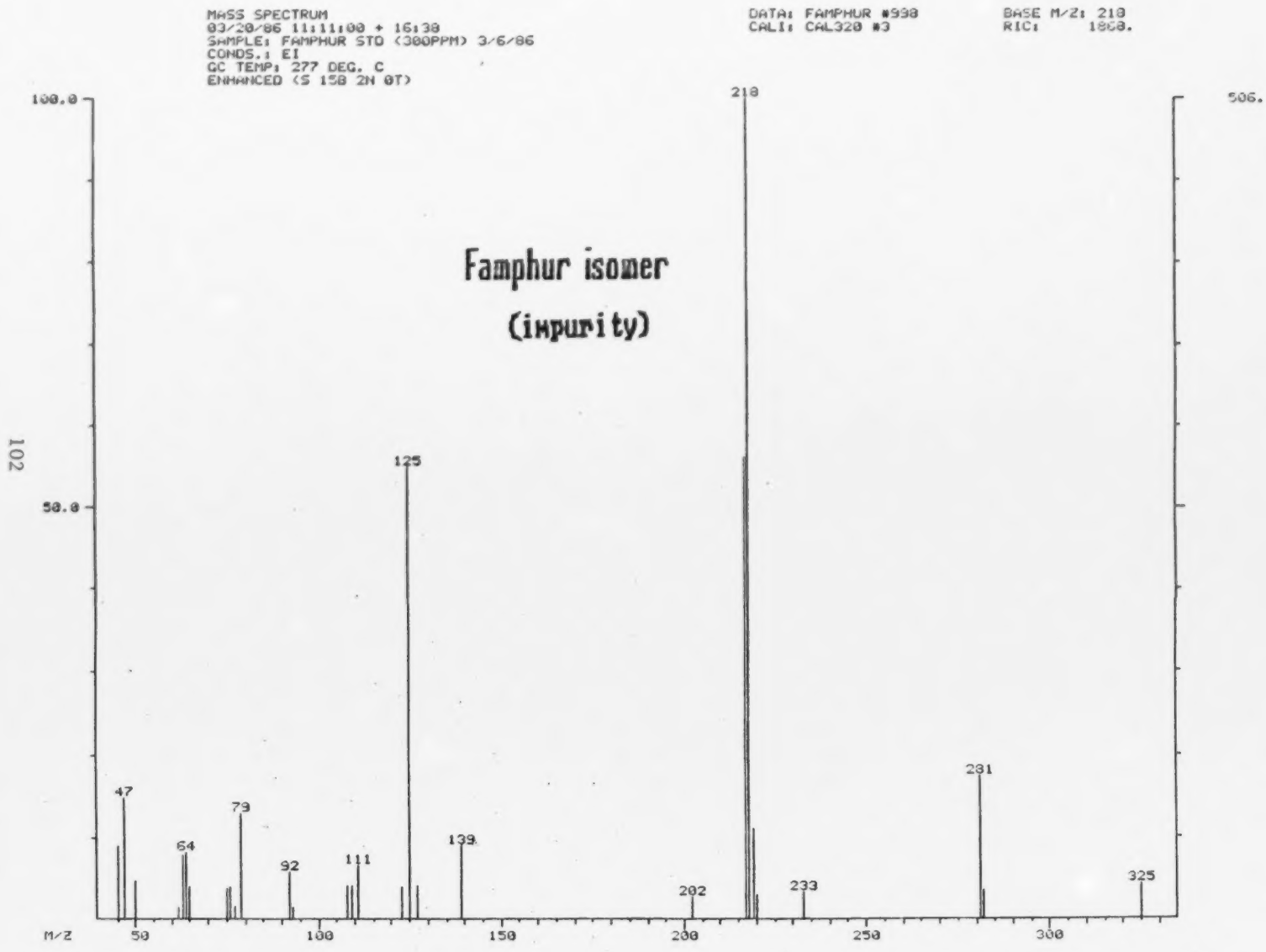
MASS SPECTRUM
03/20/86 11:11:00 + 15:41
SAMPLE: FAMPHUR STD (300PPM) 3/6/86
CONDS.: EI
GC TEMP: 265 DEG. C
ENHANCED (S 15B 2N 0T)

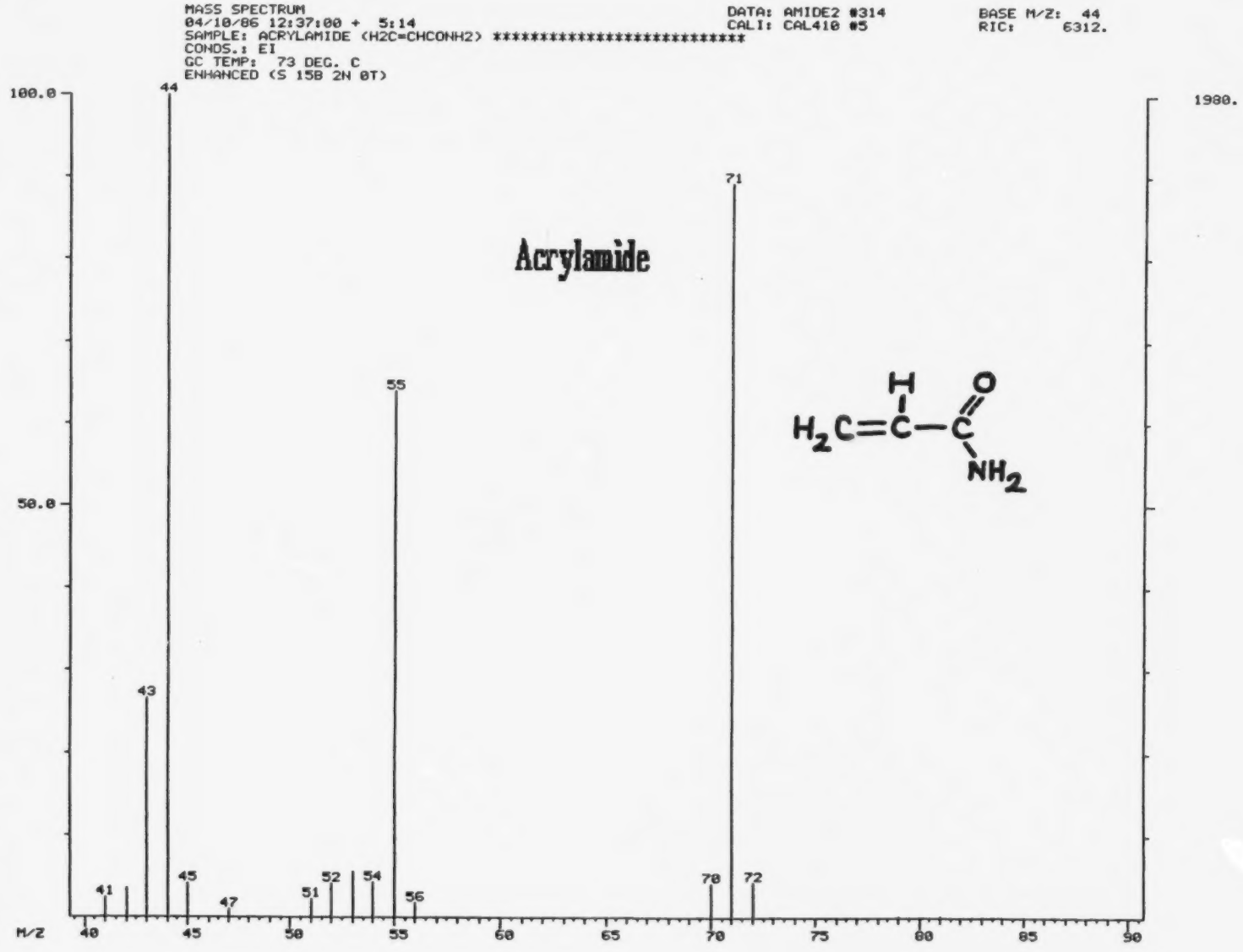
DATA: FAMPHUR #941
CALI: CAL320 #3

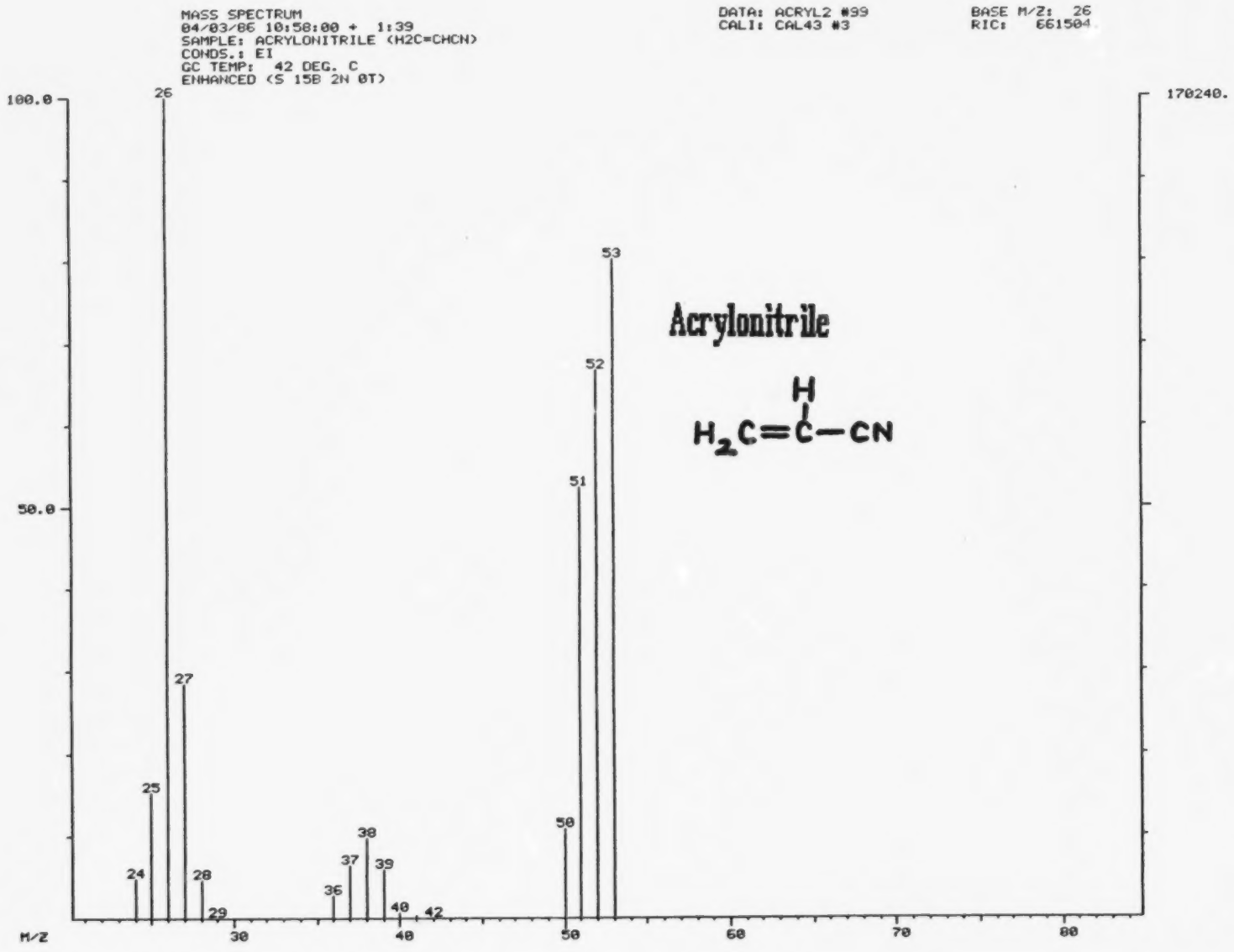
BASE M/Z: 218
RIC: 46528.



Famphur


MASS SPECTRUM
03/20/86 11:11:00 + 16:38
SAMPLE: FAMPHUR STD (300PPM) 3/6/86
CONDS.: EI
GC TEMP: 277 DEG. C
ENHANCED (S 150 2N 0T)
DATA: FAMPHUR #938
CALI: CAL320 #3
BASE M/Z: 218
RIC: 1868.
100.0
50.0
102
506.
M/Z
50
100
150
200
250
300
218
125
47
79
64
92
111
139
202
233
281
325
Famphur isomer
(impurity)

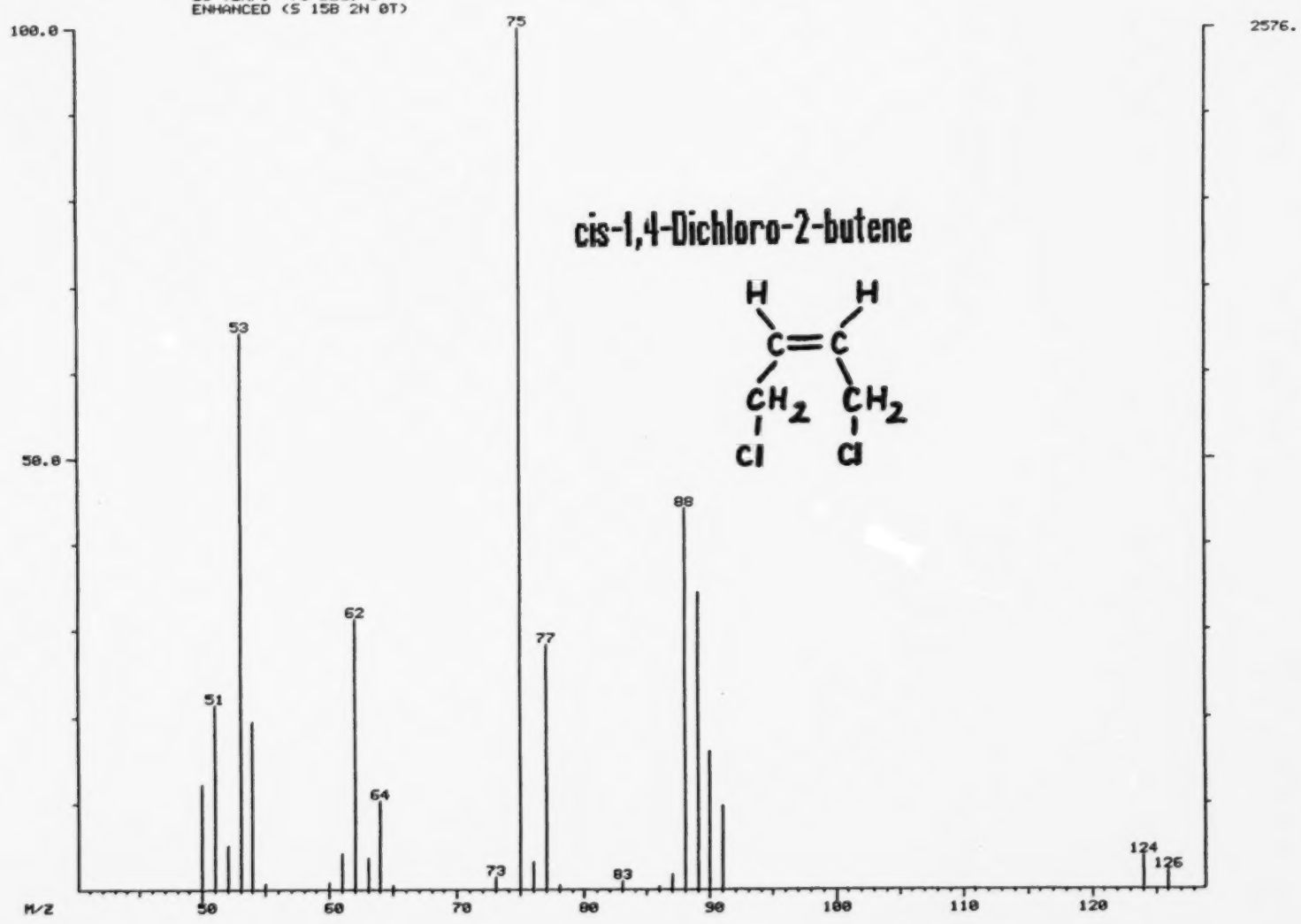

MASS SPECTRUM
04/10/86 12:37:00 + 5:14
SAMPLE: ACRYLAMIDE (H2C=CHCONH2) **********
CONDS.: EI
GC TEMP: 73 DEG. C
ENHANCED (S 15B 2N 0T)
DATA: AMIDE2 #314
CALI: CAL410 #5
BASE M/Z: 44
RIC: 6312.
Acrylamide
100.0
50.0
1980.
M/Z
40
45
50
55
60
65
70
75
80
85
90
41
43
44
45
47
51
52
54
55
56
70
71
72
H2C=CH-C(=O)-NH2


MASS SPECTRUM
04/03/86 10:58:00 + 1:39
SAMPLE: ACRYLONITRILE (H2C=CHCN)
CONDS.: EI
GC TEMP: 42 DEG. C
ENHANCED (S 15B 2N 0T)
DATA: ACRYL2 #99
CALI: CAL43 #3
BASE M/Z: 26
RIC: 661504
100.0
50.0
170240.
M/Z
30
40
50
60
70
80
24
25
26
27
28
29
36
37
38
39
40
42
50
51
52
53
Acrylonitrile
H
H2C=C—CN

MASS SPECTRUM
04/04/86 13:02:00 + 5:40
SAMPLE: CIS-1,4-DICHLORO-2-BUTENE (3-19-86)
CONDS.: EI
GC TEMP: 75 DEG. C
ENHANCED (S 15B 2N 0T)

DATA: DCBCIS #340
CALI: CAL44 #3

BASE M/Z: 75
RIC: 10832.

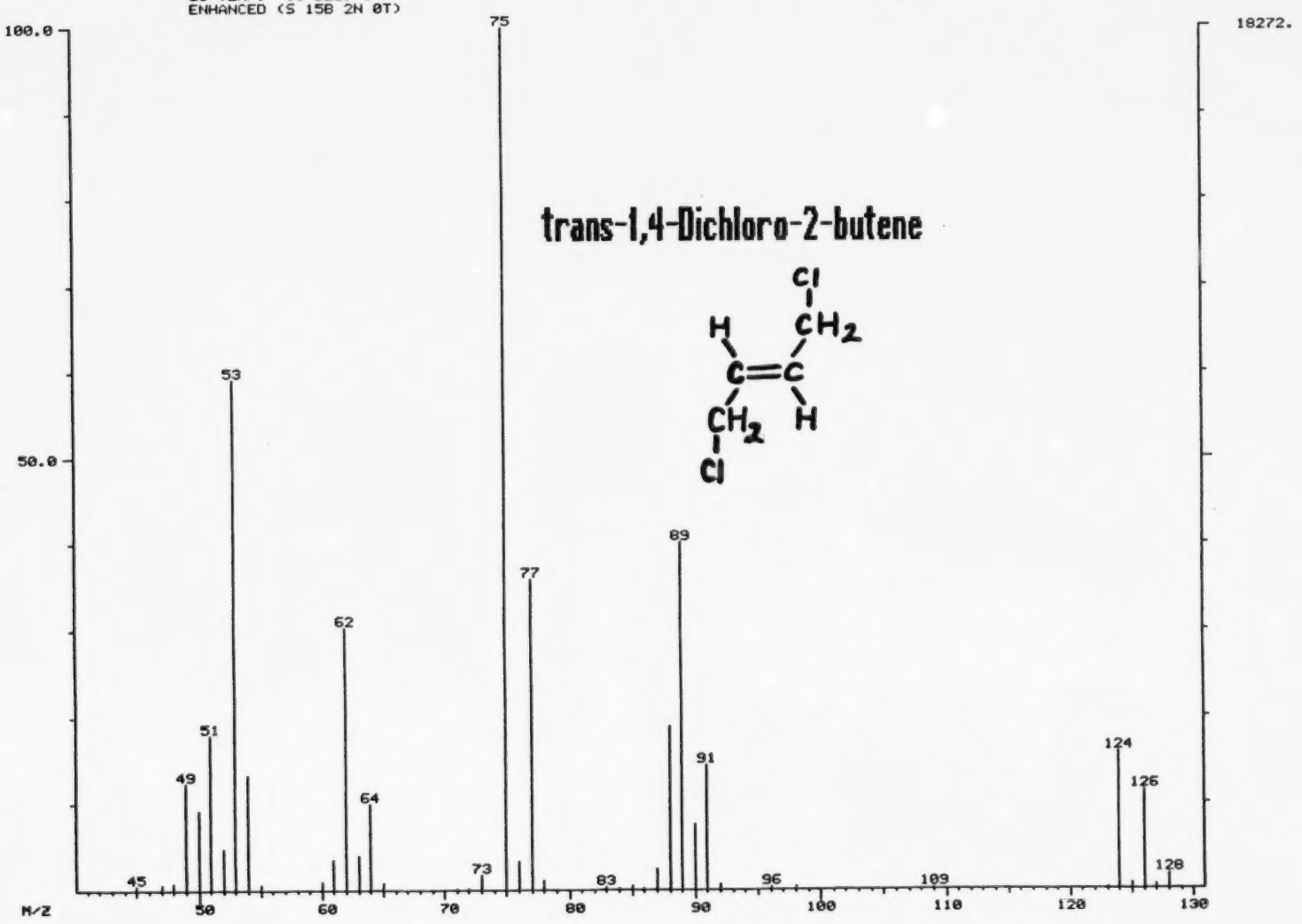


cis-1,4-Dichloro-2-butene

MASS SPECTRUM
03/20/86 14:34:00 + 4:53
SAMPLE: 1,4-DICHLORO-2-BUTENE (300PPM) 3/17/86
CONDS.: EI
GC TEMP: 86 DEG. C
ENHANCED (S 15B 2N 0T)

DATA: DCB14 #293
CALI: CAL320 #3

BASE M/Z: 75
RIC: 78336.

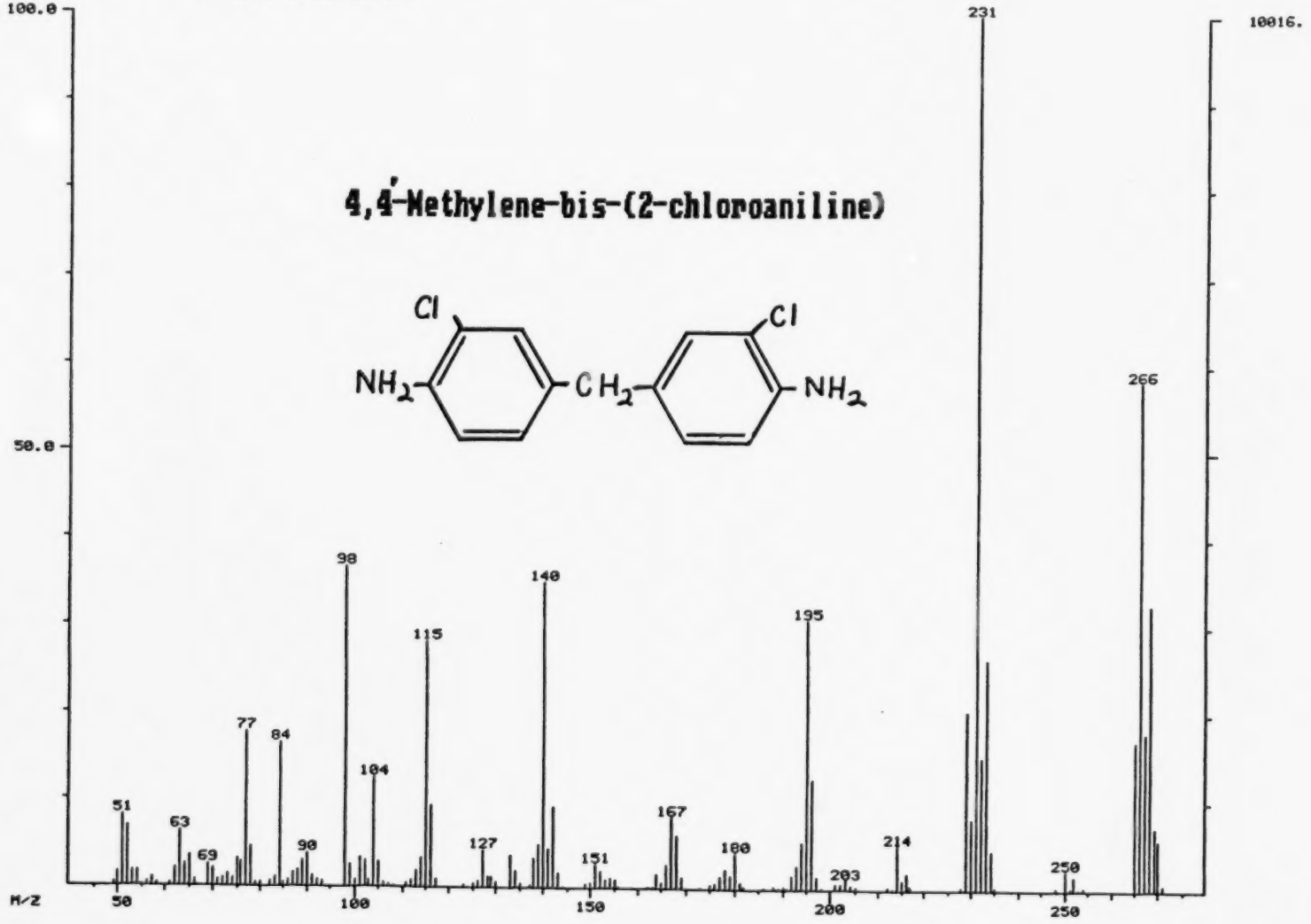


trans-1,4-Dichloro-2-butene

MASS SPECTRUM
03/20/86 10:41:00 + 16:48
SAMPLE: METHYLENE-BIS-(2-CHLOROANILINE) 300PPM 3/10/86
CONDS.: EI
GC TEMP: 279 DEG. C
ENHANCED (S 15B 2N 0T)

DATA: MBCA #1008
CALI: CAL320 #3

BASE M/Z: 231
RIC: 71808.

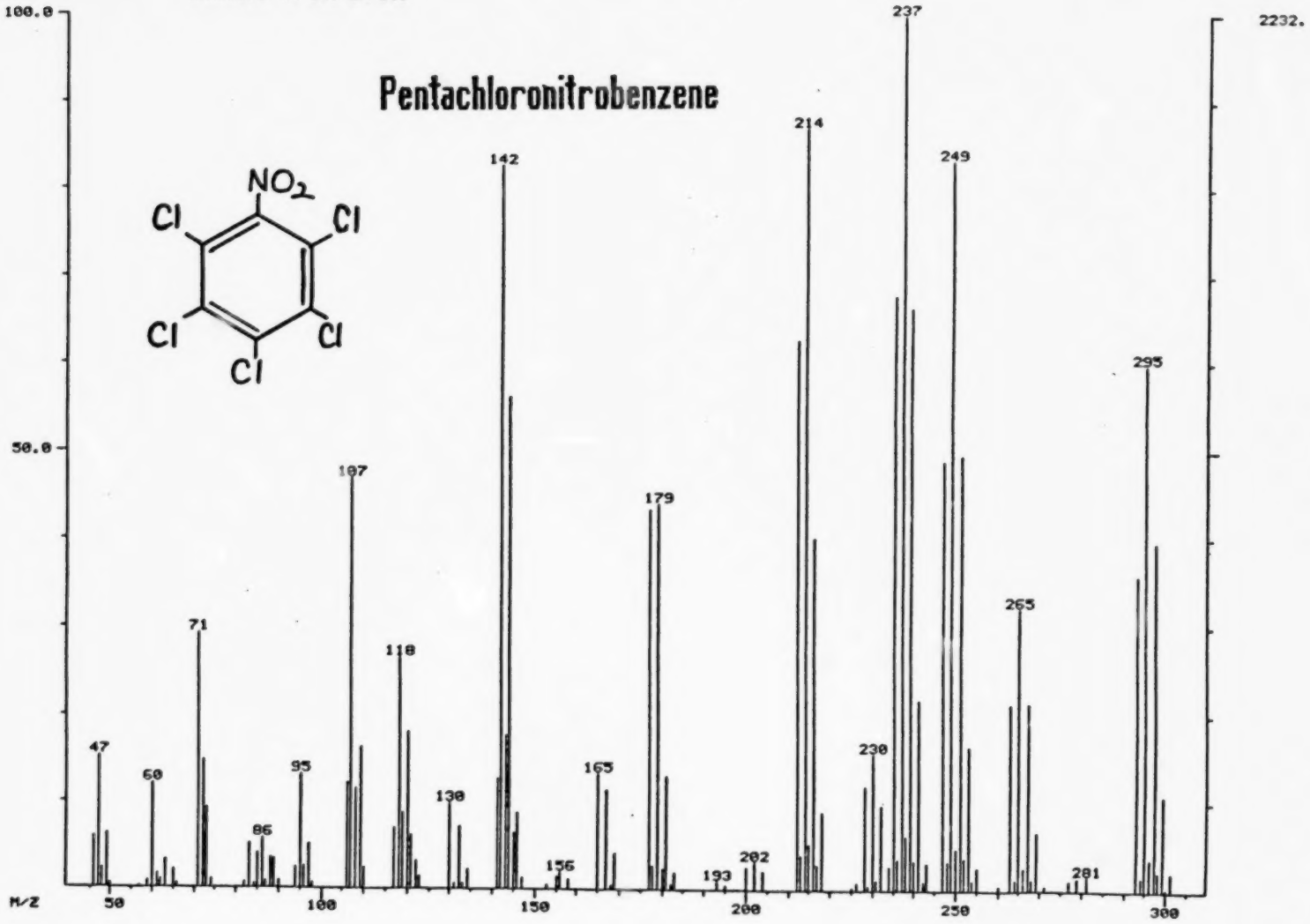


4,4'-Methylene-bis-(2-chloroaniline)

MASS SPECTRUM
03/20/86 12:37:00 + 11:06
SAMPLE: PENTACHLORONITROBENZENE STD (300PPM) 2/20/86
CONDS.: EI
GC TEMP: 210 DEG. C
ENHANCED (S 15B 2W 0T)

DATA: PCNB #666
CALI: CAL320 #3

BASE M/Z: 237
RIC: 37184.

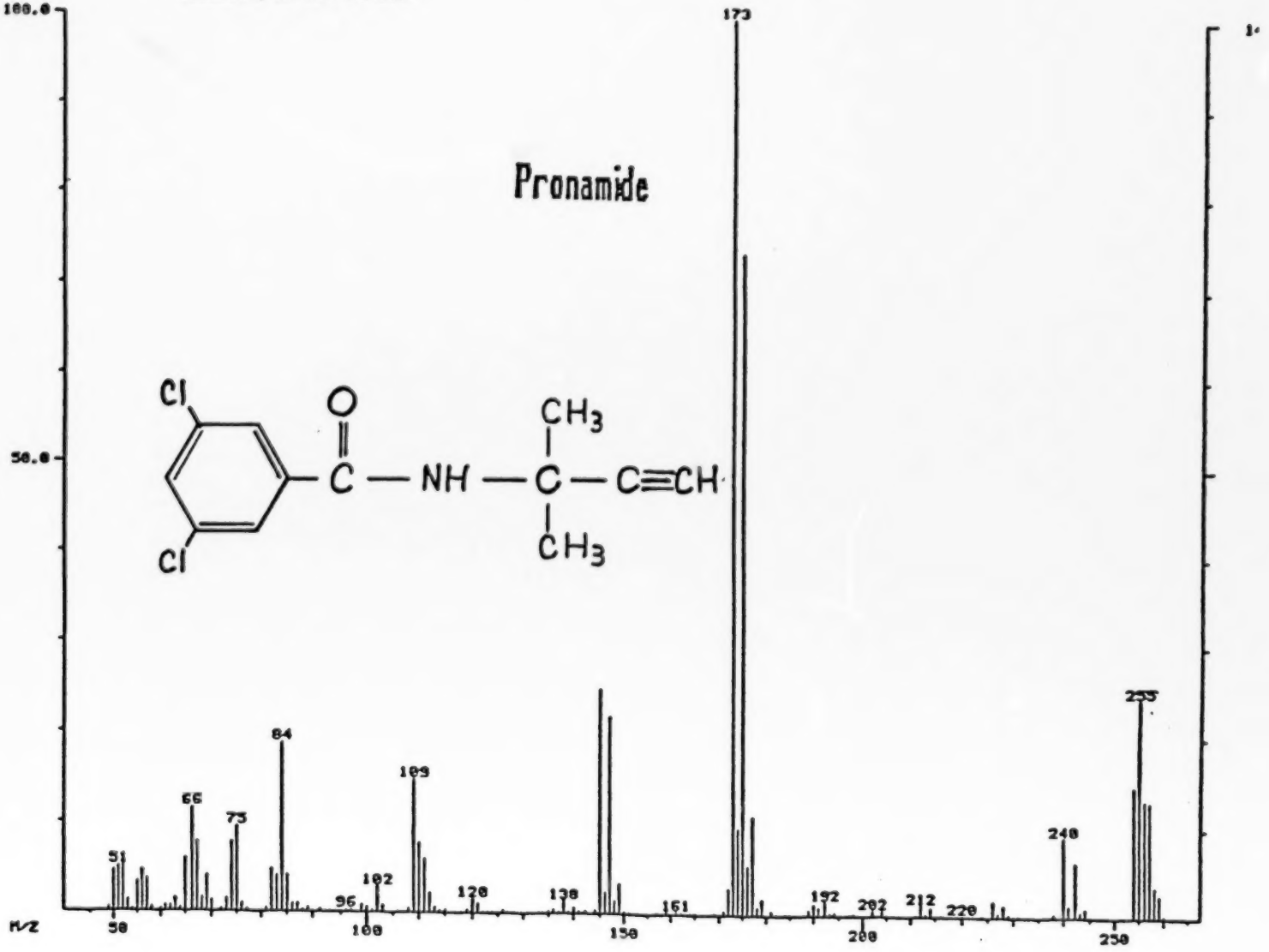


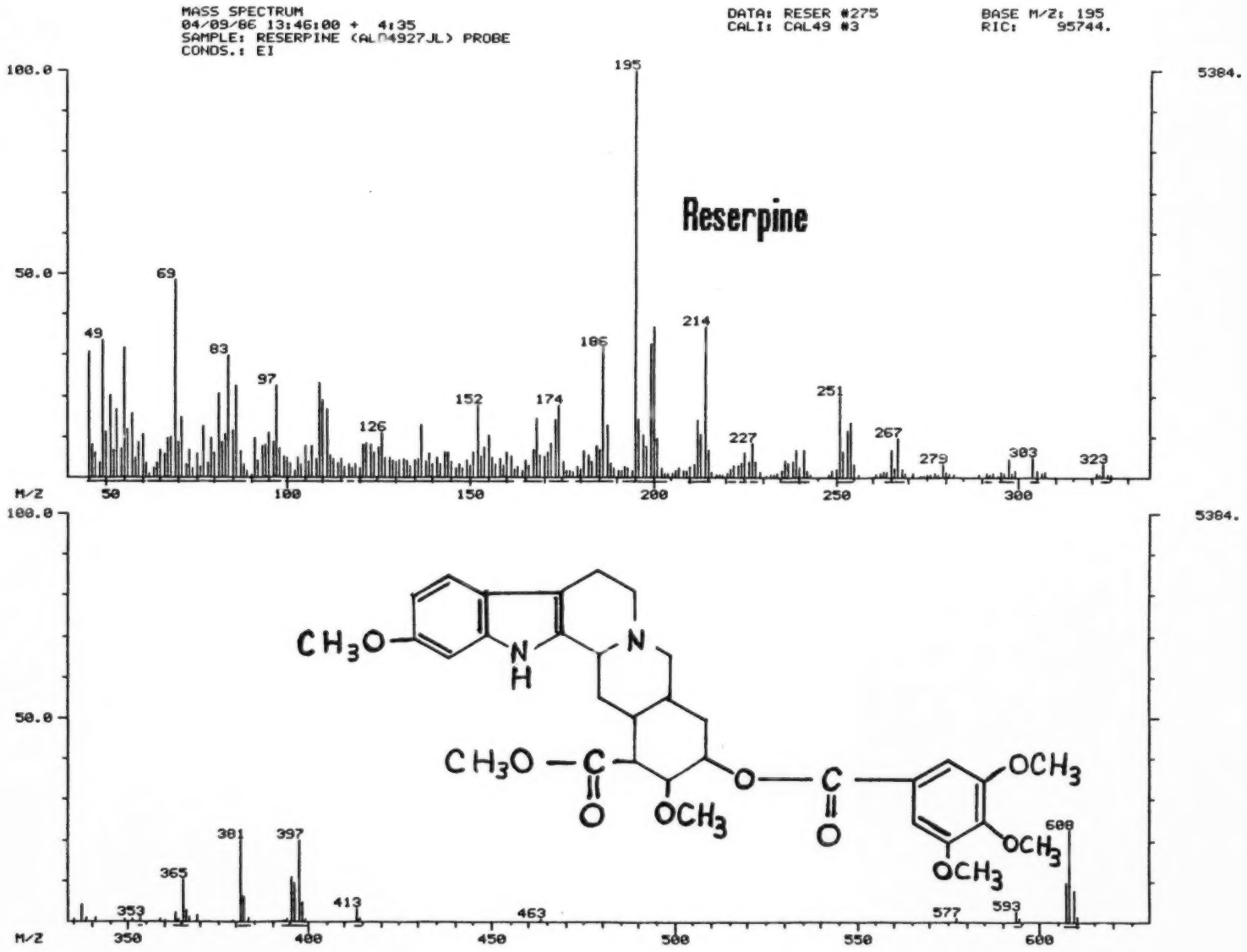
MASS SPECTRUM
03/20/86 13:01:00 + 11:07
SAMPLE: PRONAMIDE STD (300PPM) 2/20/86
CONDS.: EI
GC TEMP: 210 DEG. C
ENHANCED (S 150 2H 0T)

DATA: PRON #667
CAL: CAL320 #3

BASE M/Z: 173
RIC: 77560.

Pronamide

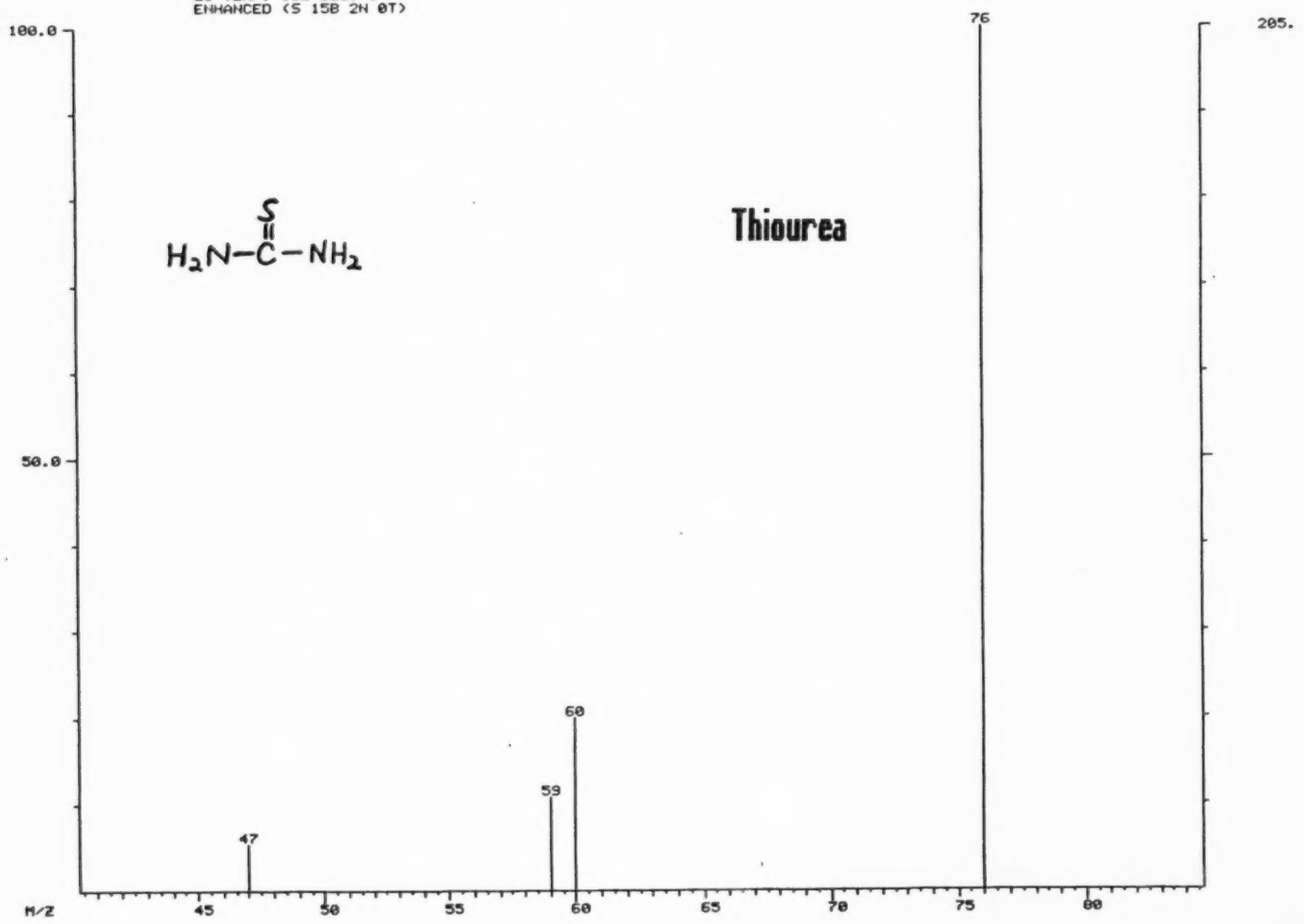



MASS SPECTRUM
04/09/86 13:46:00 + 4:35
SAMPLE: RESERPINE (AL04927JL) PROBE
CONDS.: EI
DATA: RESER #275
CALI: CAL49 #3
BASE M/Z: 195
RIC: 95744.
Reserpine
100.0
50.0
5384.
M/Z
195
69
49
83
97
126
152
174
186
214
227
251
267
279
303
323
CH3O
N
H
N
CH3O
C
O
OCH3
O
C
O
OCH3
OCH3
OCH3
381
397
365
353
413
463
577
593
608

MASS SPECTRUM
04/03/86 14:09:00 + 14:24
SAMPLE: THIOUREA (SP 3-10-86)
CONDS.: EI
GC TEMP: 162 DEG. C
ENHANCED (S 150 2N 0T)

DATA: THIOU #864
CALI: CAL43 #3

BASE M/Z: 76
RIC: 290.

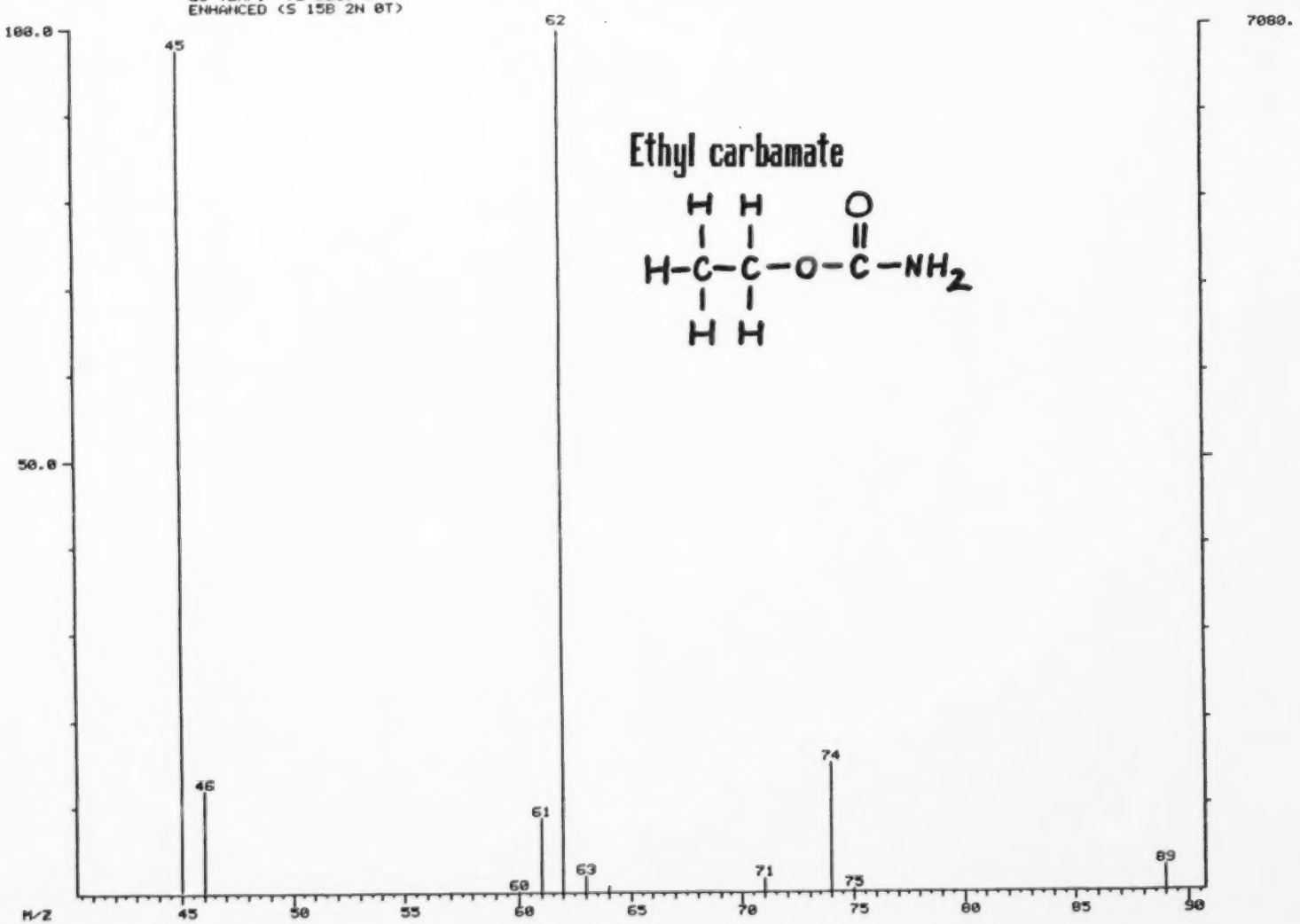


Thiourea

MASS SPECTRUM
03/20/86 14:52:00 + 3:40
SAMPLE: ETHYL CARBAMATE STD (300PPM) 3/6/86
CONDS.: EI
GC TEMP: 72 DEG. C
ENHANCED (S 15B 2N 0T)

DATA: ECAR #220
CALI: CAL320 #3

BASE M/Z: 62
RIC: 17024.

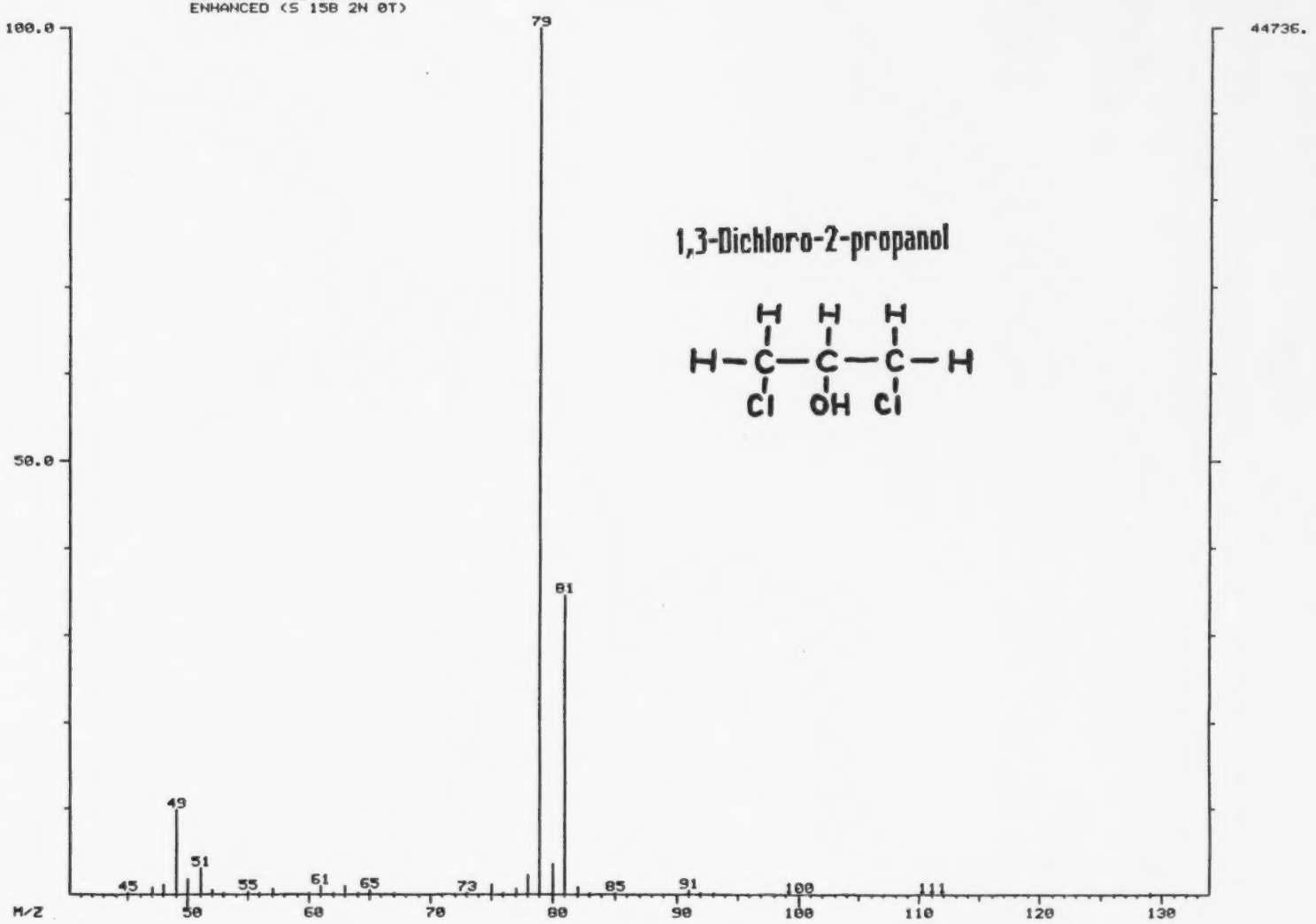


Ethyl carbamate

MASS SPECTRUM
03/20/86 14:05:00 + 4:29
SAMPLE: 1,3-DICHLORO-2-PROPANOL (300PPM) 3/12/86
CONDS.: EI
GC TEMP: 82 DEG. C
ENHANCED (S 15B 2N 0T)

DATA: DCP13 #269
CALI: CAL320 #3

BASE M/Z: 79
RIC: 74240.

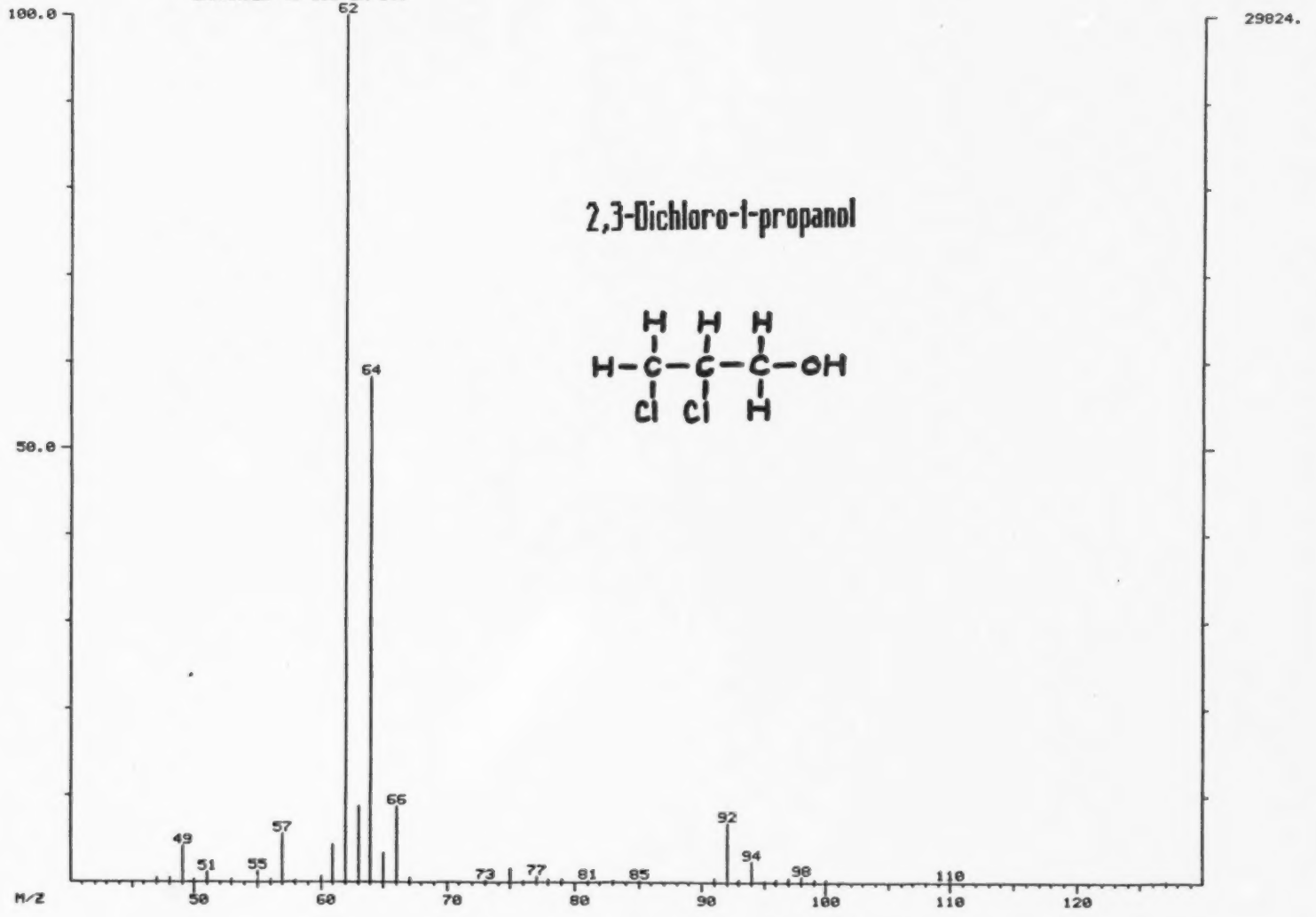


1,3-Dichloro-2-propanol

MASS SPECTRUM
03/20/86 14:22:00 + 4:53
SAMPLE: 2,3-DICHLORO-1-PROPANOL (300PPM) 3/12/86
CONDS.: EI
GC TEMP: 86 DEG. C
ENHANCED (S 15B 2N 0T)

DATA: DCP23 #293
CALI: CAL320 #3

BASE M/Z: 62
RIC: 63872.

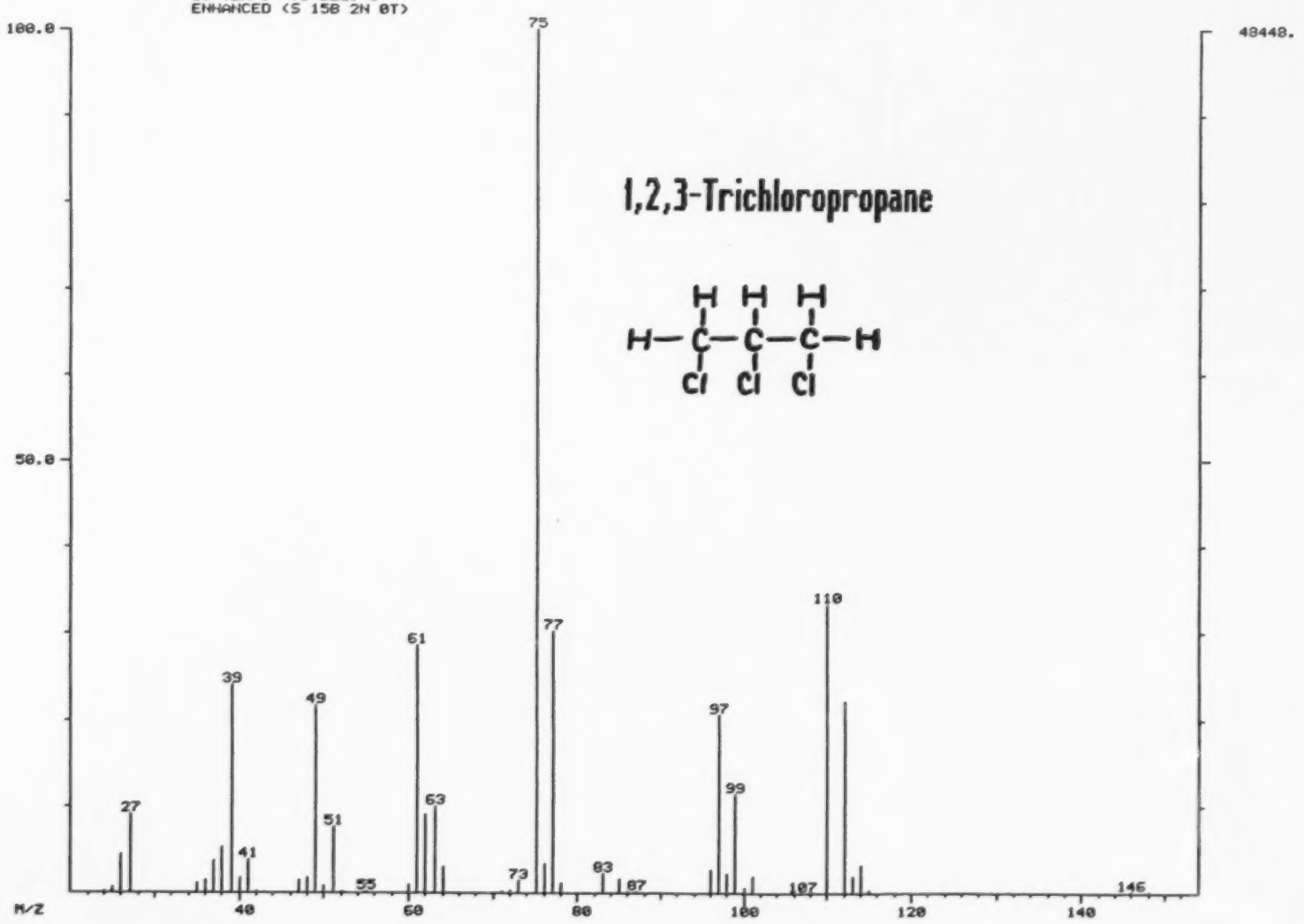


2,3-Dichloro-1-propanol

MASS SPECTRUM
04/03/86 13:52:00 + 5:57
SAMPLE: 1,2,3-TRICHLOROPROPANE (SP 4/2/86)
CONDS.: EI
GC TEMP: 79 DEG. C
ENHANCED (S 15B 2N 0T)

DATA: TCPRO #357
CALI: CAL43 #3

BASE M/Z: 75
RIC: 184832.

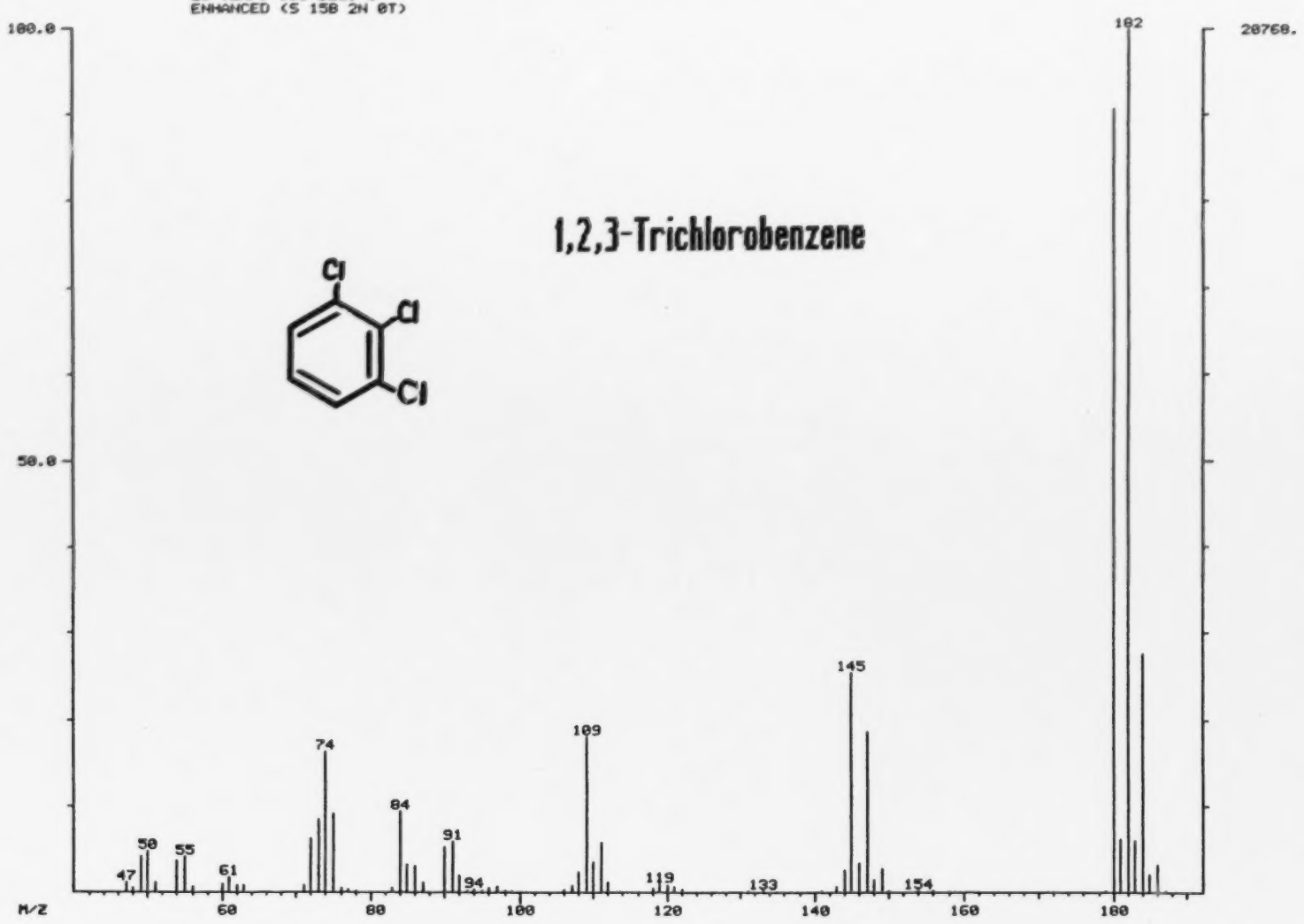


1,2,3-Trichloropropane

MASS SPECTRUM
03/20/86 13:27:00 + 5:07
SAMPLE: 1,2,3-TRICHLOROBENZENE STD (300PPM) 3/3/86
CONDS.: EI
GC TEMP: 130 DEG. C
ENHANCED (S 150 2N 0T)

DATA: TCB #307
CALI: CAL320 #3

BASE M/Z: 182
RIC: 80192.

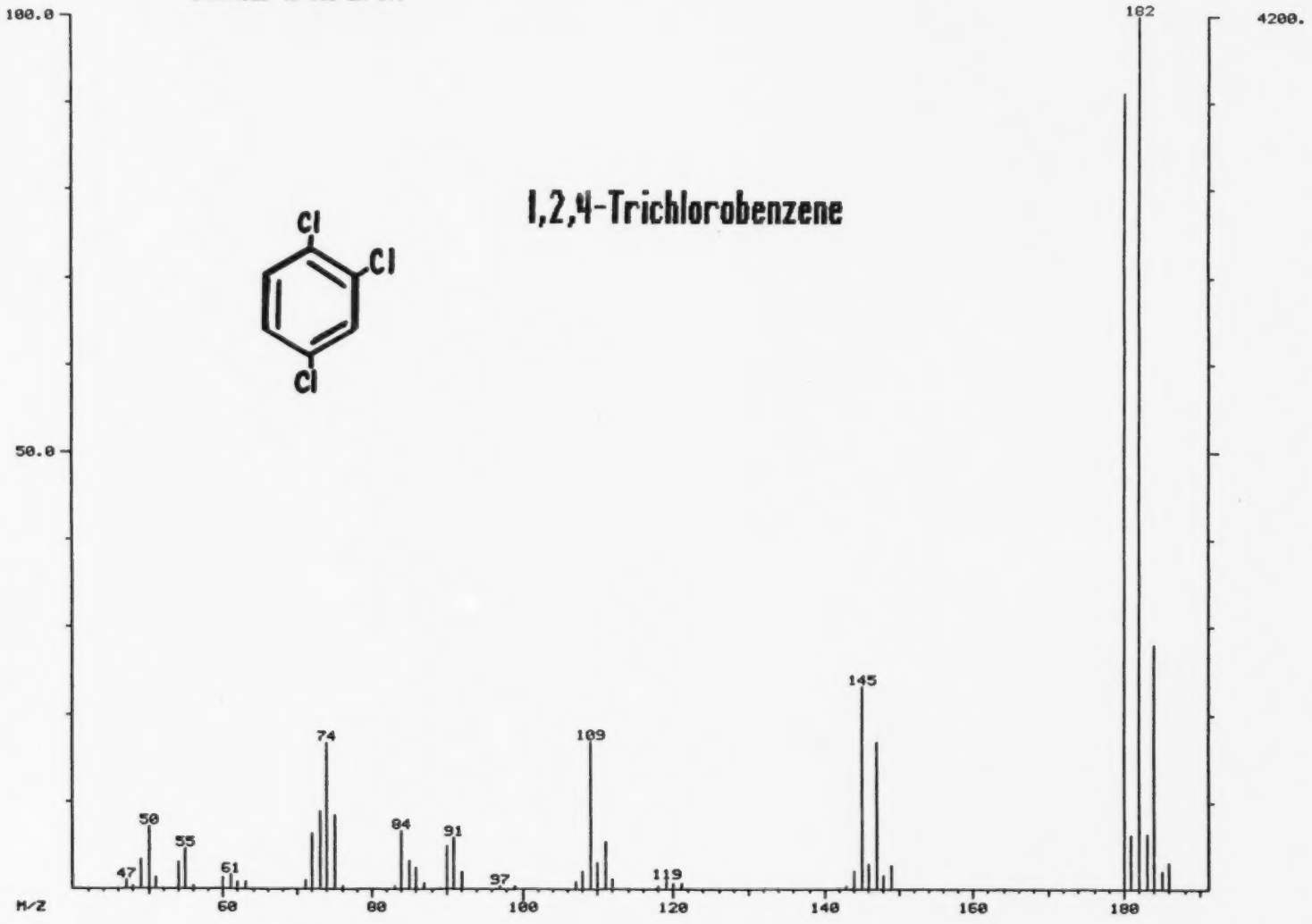


1,2,3-Trichlorobenzene

MASS SPECTRUM
03/20/86 15:34:00 + 8:22
SAMPLE: 1,2,4-TRICHLOROBENZENE (300PPM) 3/19/86
CONDS.: EI
GC TEMP: 120 DEG. C
ENHANCED (S 15B 2N 0T)

DATA: TCB124 #502
CALI: CAL320 #3

BASE M/Z: 182
RIC: 17344.



1,2,4-Trichlorobenzene

APPENDIX B

GC/FTIR ANALYSIS

Figures B1 and B2 are taken from the vapor-phase IR spectral library (EPA-LIB). The IR spectra for the positional isomers are quite different and this difference allowed verification of the 1,2,3- and 1,2,4-trichlorobenzene samples. Figures B3 and B4 contain the reference spectra and the spectra generated from the GC/FTIR analysis of the respective trichlorobenzene. From comparison of spectra a and b in Figures B3 and B4, identities are confirmed.

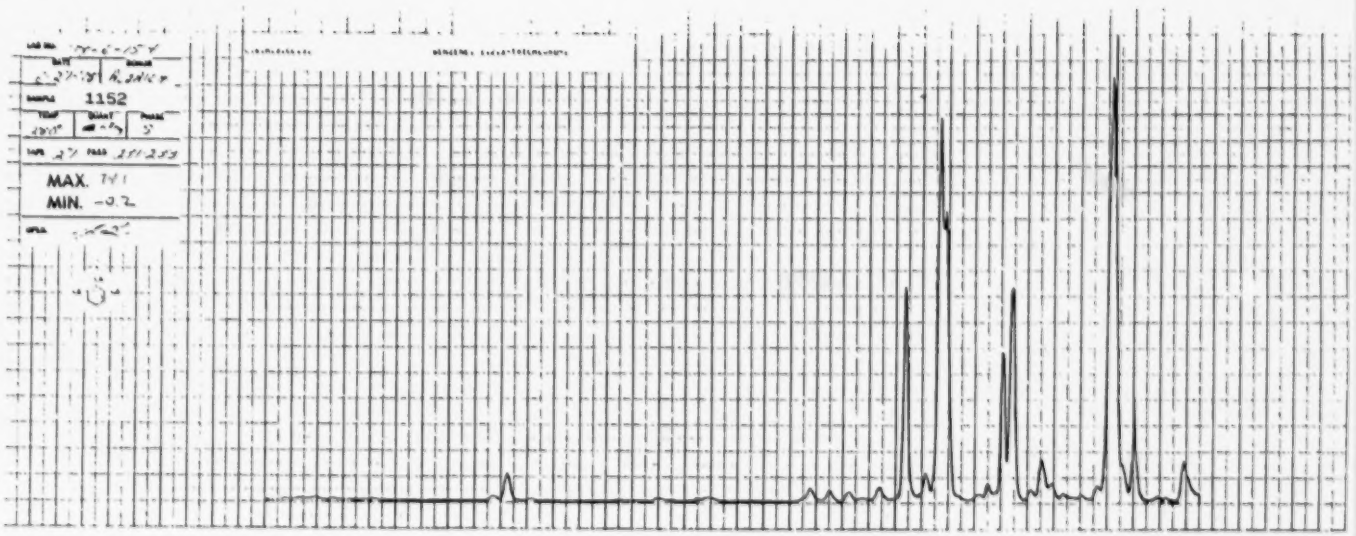
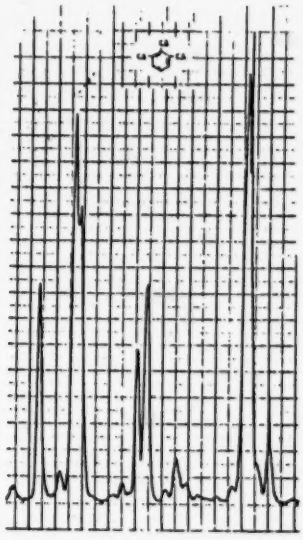
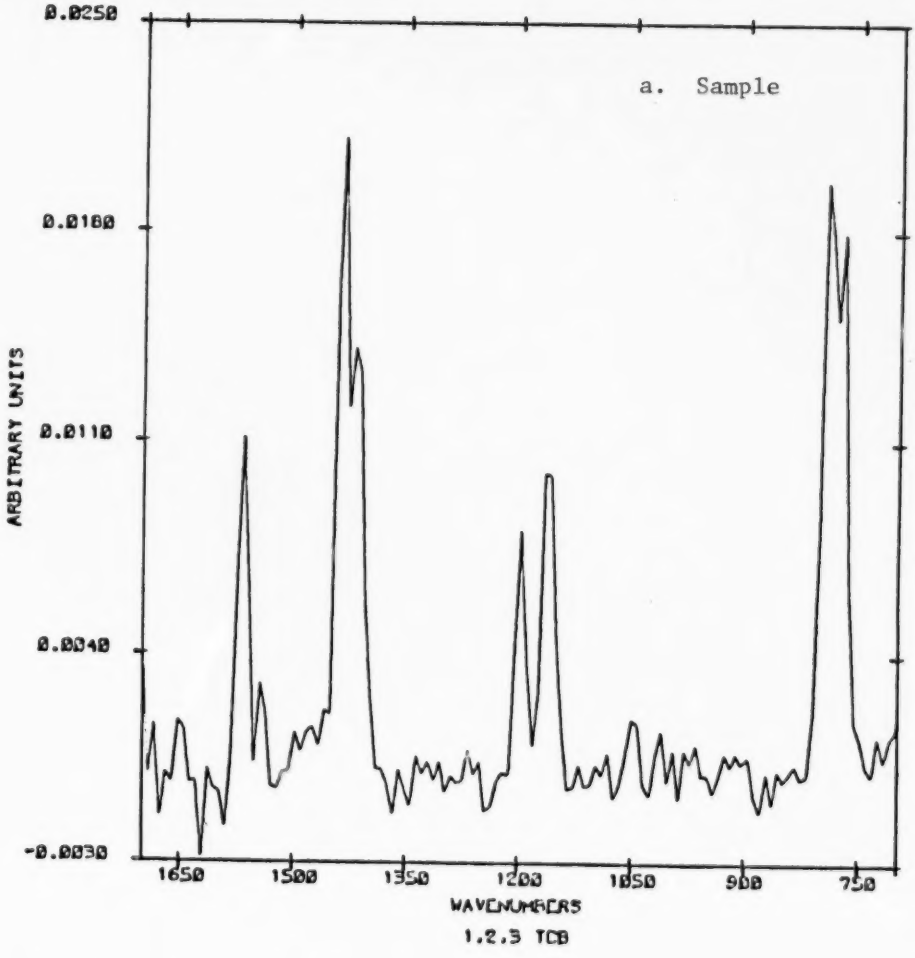


Figure B1. Reference Spectra of 1,2,3-Trichlorobenzene.

Figure B2. Reference Spectra of 1,2,4-Trichlorobenzene.

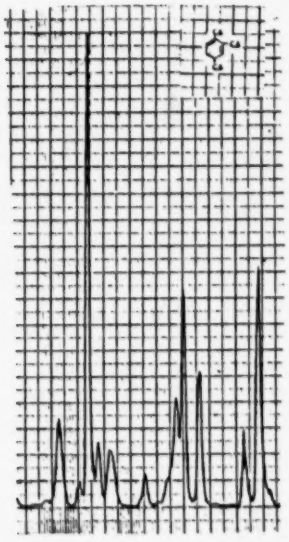


b. Reference



a. Sample

Figure B3. Infrared Spectra of 1,2,3-Trichlorobenzene.



b. Reference

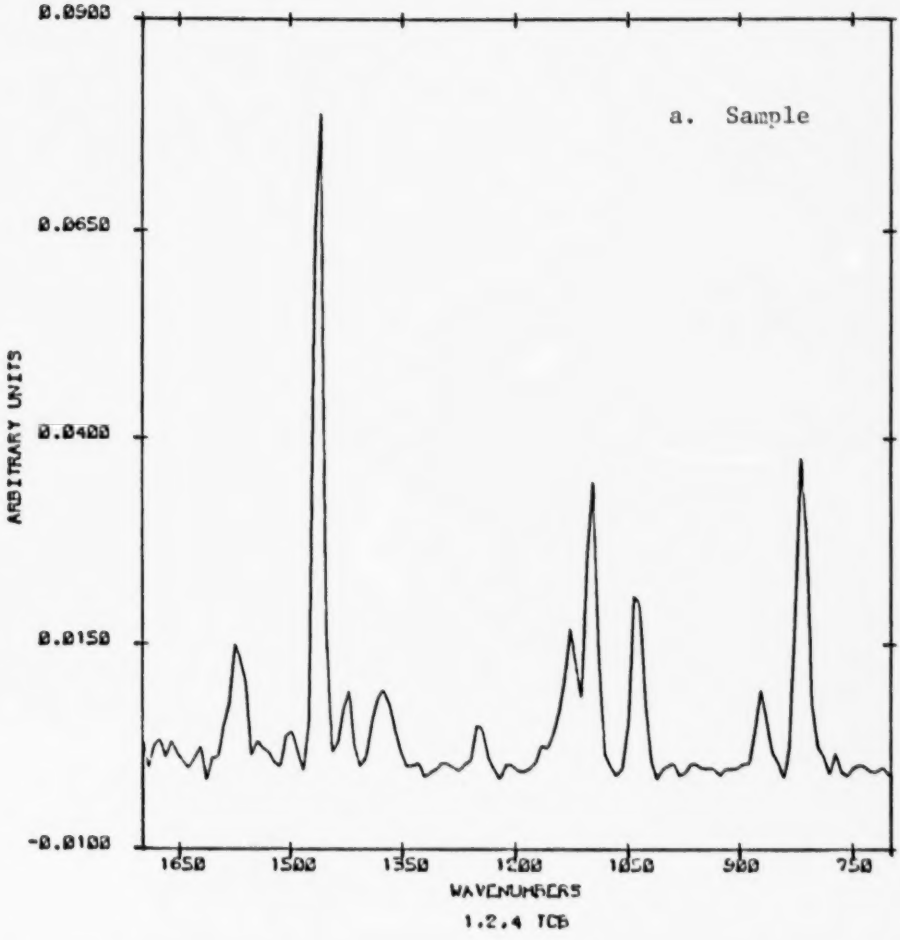


Figure B4. Infrared Spectra of 1,2,4-Trichlorobenzene.